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Evaluating CEN/TS 12390-9 To Assess Concrete for UK Freeze-Thaw Exposure Conditions

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Evaluating CEN/TS 12390-9 To Assess Concrete for UK Freeze-Thaw Exposure Conditions

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Declaration

I hereby declare that I am the author of this thesis, and that the work of which this thesis is a record has been composed by me, that all references have been cited have been consulted, and that it has not been previously presented for a higher degree.

Christopher Hynard

Certificate

This is to certify that **Christopher Hynard** has completed research under my supervision, and that he has fulfilled the conditions of Ordinance 14 of the University of Dundee, so that he is qualified to submit this thesis in application for the Degree of Doctor of Philosophy.

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Abstract

Over the past 20 years, winters in the UK have become milder with the odd harsh winter and with the drive to use low carbon cements, questions have arisen over the performance of these concretes in freeze-thaw environments. This research project investigated the influence of cement type on concretes subjected to freeze-thaw conditions and the correlation between the microstructural properties of concrete and freeze-thaw performance using the CEN/TS 12390-9. The test method based on SS 137244 with a temperature profile of +20±4°C to -20±2°C and the results were compared to a scaling loss of up to 1.0 kg/m^2 (deemed *Acceptable* performance).

Concretes were manufactured with CEM I, CEM II/B-V (fly ash), CEM III/A (GGBS) and CEM II/A-L (limestone) cements, both non-air and air entrained, with different target strengths (20-60 MPa for non-air entrained and 20-50 MPa for air entrained) and a target air content of 4.5%, in accordance with BS 8500. BS EN 197-1 outlines the maximum addition contents that can be used in concretes and BS 8500 describes lower maximum limits for these additions regarding freeze-thaw conditions. CEM II/B-V (45%, 55% and 65%), CEM III/A (65%, 75%, and 85%) and CEM II/A-L (30%, 40% and 50%) were tested with addition contents higher than the allowable limits to determine how these influence the air void characteristics and freeze-thaw resistance. Concretes were analysed to determine the effects of air entrainment on the air void characteristics (air content of hardened concrete, spacing factor, specific surface, void frequency average chord length and microair content) and subsequent freeze-thaw resistance. The study also examined the effect of cement type in concretes with a range of target air contents (7.0%, 9.5% and 12.0%).

Powers (1945) derived the Spacing Factor parameter to determine if a concrete could resist freeze-thaw whereby voids within the concrete were less than 250 µm apart. Development of 3rd generation superplasticizers combined with air entrainers, both air and non-air entrained concretes had a spacing factor value less than 250 µm (and for most concretes <100 µm), however many of the non-air entrained concretes did not achieve an *Acceptable* scaling rating showing that Spacing Factor cannot be used as an initial assessment of freeze-thaw resistance. Other parameters including the specific surface and void frequency should be considered when determining freeze-thaw resistance as these provide better correlation with performance. For non-air entrained concretes void frequency should be <0.600 mm^{-1} and where air entrainment is used, >0.600 mm^{-1} is acceptable.

All air entrained concretes (target air content 4.5%) achieved an *Acceptable* scaling rating even with the varied cement type and target compressive strength. Non-air entrained concretes with a strength 40 MPa or less did not achieve this rating, and a 60 MPa CEM II/B-V concrete was not able to withstand freeze-thaw damage. Higher air contents were shown to protect the concretes, however there was a plateau point where the air entraining admixtures changes from increasing the air content to altering the workability like a superplasticizer but it did increase the freeze-thaw resistance with a maximum compressive strength loss of up to 25% for some cement types. Increasing the addition content above the maximum decreases the compressive strength. Despite the fact the compressive strength decreased with increased addition contents, the concretes were still able to achieve an *Acceptable* scaling rating. BS 8500 also states that a lightweight aggregate concrete can perform well in XF4 exposure conditions. This was studied to understand the microstructural properties and whether the aggregate replicates an air entrained concrete in terms of air void size and distribution, and to that end it was observed that lightweight aggregate results were like air entrained concrete.

CEN/TS 12390-9 is based on the Swedish Standard 137244 for freeze-thaw resistance and compared to the UK, these temperatures are rarely seen. Different temperature ranges (+13°C to -13°C and +18°C to -8°C) were considered to reflect the temperatures more seen in the UK highlighting that for a concrete to be warmer (but still below 0°C) for longer, produced more scaling than CEN/TS 12390-9 temperature profile. Moreover, other environmental factors are not considered in the test including the effects of carbonation since concrete is exposed to carbon dioxide all year round then this can potentially influence a concrete's resistance and found higher scaling loss for carbonated, non-air entrained concretes, in particular CEM II/B-V and CEM II/A-L concretes with a loss of 12.35 kg/m^2 and 11.07 kg/m^2 respectively. Increased salt concentration from multiple applications was studied to determine how increasing the salt levels (from the standard 3% to 6%, 9% and 12%) would affect the concrete's durability. Observed was the change in freeze-thaw mechanism between 6% and 9% from surface scaling to internal freeze-thaw cracking.

Contents

List of Tables

List of Figures

Chapter 1
Research Project Introduction

1.1 Background

The concrete industry is the life blood of the construction sector with every building, tunnel or bridge using concrete in one way or another. Within the UK, the construction industry as a whole accounts for 13% of the UK economy, including construction related products, services, contracting accounts and providing employment of around 3 million people (HM Government, 2013). In 2013, the UK Government produced a new strategy improve sustainable construction whilst lowering costs and emissions and improving the rate of construction completion.

With the need to push the boundaries of concrete construction while simultaneously reducing the carbon footprint more focus, globally, has been to the use of waste material, not just from the construction industry but from the coal and iron industries. Industrial by-products, such as fly ash (FA) from coal fired power stations and ground granulated blast-furnace slag (GGBS) from the iron industry, have been observed to maintain and possibly improve a concrete's properties whilst being able to achieve the sustainable construction required to reduce the global carbon footprint. Combining standard CEM I (CEM I) with the waste products has permitted a significant drop in the use of CEM I in concrete causing a positive domino effect resulting in a reduction in the carbon dioxide (CO_2) produced during the manufacturing process of cements. Integrating waste material in current concrete specification has opened new avenues and provided a wide range of various concretes which has led to these concretes to be standardised, BS EN 197-1: 2011 (Newlands, 2001; BSi, 2011a). Table 1.1 outlines the twenty-seven different cement types that are used in the UK with cements such as sulphate resisting, and early low strength now being employed.

By the end of 2013, it was estimated that the construction industry contributed £90 billion in revenue to the UK economy which equates to approximately 7% of the total UK economy, whereby £550 million was spent on repair and maintenance of existing structures. Concrete, specifically reinforced concrete, is currently the most widely used material in construction and while it is cheaper and stronger, problems do arise as to its durability aspects. Given that most of the structures in the UK mainly use concrete as the construction material, there are many durability factors that are identified and considered when specifying concrete for a particular situation. Traditionally, concrete was designed for a purpose where it would be cast for a structure and then left to carry out its design life. However, this 'design' has long changed with the introduction of Eurocodes and European based design standards which look to implement more sustainable construction whilst at the same time place more focus on the deterioration mechanisms and designing to either significantly reduce the effects on the materials or protect the elements against them all together.

Table 1.1 Cement types available for structural concrete in accordance with BS EN 197-1 Cement types available for structural concrete in accordance with BS EN 197-1

Cement Type	**Notation of Cement Type**	**Composition Content, %**	
		Clinker	Other Constituents
CEM I	CEM I	95-100	-
Portland-Slag Cement	CEM II/A-S	80-94	6-20
	CEM II/B-S	65-79	21-35
Portland-Silica Fume Cement	CEM II/A-D	90-94	6-10
Portland-Pozzolana Cement	CEM II/A-P	80-94	6-20
	CEM II/B-P	65-79	21-35
	CEM II/A-Q	80-94	6-20
	CEM II/B-Q	65-79	21-35
Portland-Fly Ash Cement	CEM II/A-V	80-94	6-20
	CEM II/B-V	65-79	21-35
	CEM II/A-W	80-94	6-20
	CEM II/B-W	65-79	21-35
Portland-Burnt Shale Cement	CEM II/A-T	80-94	6-20
	CEM II/B-T	65-79	21-35
Portland-Limestone Cement	CEM II/A-L	80-94	6-20
	CEM II/B-L	65-79	21-35
	CEM II/A-LL	80-94	6-20
	CEM II/B-LL	65-79	21-35
Portland-Composite Cement	CEM II/A-M	80-88	12-20
	CEM II/B-M	65-79	21-35
Blast Furnace Cement	CEM III/A	35-64	36-65
	CEM III/A/B	20-34	66-80
	CEM III/A/C	5-19	81-95
Pozzolanic Cement	CEM IV/A	65-89	11-35
	CEM IV/B	45-64	36-55
Composite Cement	CEM V/A	40-64	36-60
	CEM V/B	20-38	62-80

The most fundamental issue for a designer is the understanding of the environment in which the concrete will have to endure, tied with the concrete's durability performance under different environmental factors. This means that the designer has a responsibility to ensure that the concrete specification must fit the desired performance so that the concrete withstands the harshest of environmental conditions. Concrete design and specification are tied to the Exposure Class as defined in the CEN standards (European Standards) where the constant development of BS EN 206-1 defines a simple, generic concrete design which suits all European countries. EN 206 is more like a series of guidelines used by each country to create their own standards from it. In the UK, the complementary standard for BS EN 206-1 is BS 8500, which is a performance-based specification depending on the chosen Exposure Class.

Testing in the concrete industry is based upon results that are repeatable and reproducible and in concrete these are few and far between. Establishing destructive testing for such a vastly used material is imperative and can potentially reduce the deterioration mechanisms from a range of concrete durability issues associated with the external environment. Achieving such results is difficult, so continual development of standardised destructive testing must be done before performance-based specification can be tested.

A serious destructive phenomenon affecting a concrete's durability performance is freeze-thaw of concrete, particularly in those which are not air entrained. The infiltration of water and salt agents into the concrete voids, coupled with the change in the temperature, results in the water freezing in the voids and expanding, exerting pressure on the pore walls. This exertion causes the formation of cracks leading to more water infiltrating the concrete, thus more cracking. A continuous cycle then forms until the inevitable failure of the concrete element. Most of the infrastructure is built using concrete as the bulk material including tunnels, bridges and dams in some form whether that be the entire structure or just simply the foundations, all have the potential to succumb to freeze-thaw attack.

Freeze-thaw attack has long been studied due to its destructive nature yet, the root cause of this phenomenon is still unknown. However, what is known is there are two different deterioration mechanisms that for freeze-thaw, internal frost damage and freeze-thaw salt scaling. There is a general assumption that both mean the same thing, and both cause the same amount of damage, this research distinguishes between them highlighting the differences and the test methods for both. To prevent this deterioration, it is common practice to do one of two things, either increase the strength of the concrete or to include air entrainment in the design. The latter being the better option as it ties in with the sustainability agenda set out by the EU and it is proven to provide better freeze-thaw protection.

Figure 1.1 illustrates the deterioration of a footpath from freeze-thaw on concrete when it is not fully protected and under constant loading/use and Figure 1.2 shows internal freeze-thaw damage when combined with another deterioration process such as carbonation induced corrosion.

Figure 1.1 Scaling of a concrete pavement. Continuous freezing and thawing with constant foot traffic has removed the top surface of the concrete.

Figure 1.2 Internal freeze-thaw damage combined with carbonation induced corrosion of a bridge abutment

The problem with the sustainability agendas, particularly those using by-products to reduce waste, is that despite the fact that majority of concrete requires a certain percentage of CEM I, there is unknown data as to whether these cement types outlined in BS EN 197-1 are capable of withstanding freeze-thaw attack. BS EN 206-1 and BS 8500 both specify significantly more aggressive conditions in each Exposure Class that determines the validity of a cement addition and the content percentage. With all deterioration mechanisms, the time taken for a concrete to show signs of distress depends on several factors like the bulk engineering properties including water/cement ratio and compressive strength but also the external environment. For freeze-thaw, this can be a slow process where continuous freezing and thawing of the solution eventually shows cracking on the surface or the top layer of the concrete is scaled off rather quickly.

The freeze-thaw test method for concrete is designed to put concrete through a very harsh process whereby temperatures are rarely reached in the UK. Weather and temperature data show that the winters are becoming milder resulting in less need to test concrete to the absolute extremes when these temperatures are not reached. This creates an ideal situation whereby the test method can be improved to suit the UK climate and better designed concretes for a longer design life in freeze-thaw conditions.

1.2 Scope of Study

CEN/TS 12390-9 is the test method used to analyse concretes for freeze-thaw conditions. This method has been developed from the Swedish test method, SS 137244, where concretes are subjected to 56 cycles of cycling temperatures between +20°C to -20°C ±4°C. This study aims to analyse different cement types and how air entraining admixture influence the microstructural properties of the concrete, thus, the freeze-thaw resistance. After examination of the freeze-thaw test method it had been identified that there is potential development in the test method. A detailed test programme of laboratory conditions showed the need for the freeze-thaw test method to be upgraded for more realistic representation of real-world conditions including but not limited to temperature, salt concentration and the influence from carbonation.

The performance of cements less used in the UK, particularly for freeze-thaw resistance, were considered. Materials including fly ash (FA), ground granulated blastfurnance slag (GGBS) and limestone were examined to determine the influence on the air void characteristics in relation to the freeze-thaw resistance and ensuring that replacement values were in accordance with BS EN 197-1 and BS 8500. Furthermore, the addition content was increased beyond the limit stated in BS 8500 and freeze-thaw tested to determine whether and how a further increase in the content changed the durability performance.

Whilst both air and non-air entrained concretes were tested with various cement types the air contents were increased to observe the air void changes compared to the standard air content defined in BS 8500. This increase in the air content was also tested for freeze-thaw considering whether the increase provided ‘more’ protection in terms of reducing the scaling loss compared to the concretes produced in accordance with BS 8500.

Each concrete was physically analysed using an air void analyser to determine the microstructural properties such as the spacing factor, specific surface, void frequency, average chord length and microair content. These characteristics were coupled with the results of the freeze-thaw salt scaling to understand the microstructural build-up of the concrete and to identify markers which can be used to determine initial scaling rate and possible limit point.

Focus was then placed on concretes containing lightweight aggregate as preliminary findings (analysis conducted on existing lightweight aggregate concrete structure) found that this material created its own form of air entrainment due to the high void count seen from testing. This material separated from the conventional aggregates used in concrete as with its high absorption rate prevented the ingress of water and salts into the concrete by way of a sacrificial aggregate protecting the cement paste and allowed water to move more freely through the concrete, even during the freezing cycle.

Whilst the cement type used in concrete has been reviewed rigorously throughout this project it was observed that the test method itself provided significant problems during the preparation and testing of the concretes but also errors in the results. Changes were made to the testing parameters to determine a more suitable combination which would closely represent the UK climate seen today, from the temperature envelope to the increase in salt concentration closely representing the increase in concentration from the continuous applications of grit salt to resist ice build-up, to the inclusion of carbonation during the freeze-thaw testing to replicate the concretes conflict against these two mechanisms at the same time as one failure mechanism does not work alone.

1.3 Aim and Objectives

The aim of the project is to investigate the CEN/TS 12390-9 method and associated acceptance criteria as means of evaluating air-entrained concretes or equivalent for use in UK exposure conditions. The following objectives have been set to meet this aim:

I. Establish the range of materials for and suppliers of the test concretes for the investigation. These will include concretes containing fly ash, GGBS and limestone all with freeze-thaw resisting aggregates. Carry out F/T scaling tests following the CEN/TS 12390-9 (3.0% NaCl) method to determine the performance of the test concretes.

II. Use an automatic image analysis system and follow the BS EN 480-11 and ASTM C457 measurement methods, to quantify the air void characteristics of the test concretes.

III. Analyse the recommended concretes for XF4 Exposure Class to determine how resistant these concretes are to freeze-thaw, in particular to compare concretes containing lightweight aggregate with other XF resisting aggregates.

IV. Analyse the data from the study to examine various issues about estimating F/T damage (from fresh air content/air void characteristics), rates of deterioration within and between concretes, and comparisons between laboratory and field behaviour.

V. Identify suitable test conditions/performance criteria for modifying the CEN/TS 12390-9 method, for example effect of carbonation, or temperature profile representing real time deterioration to achieve a particular mass loss, as appropriate.

1.4 Hypotheses Tested in Research Project

During this research several hypotheses were derived and tested to determine specific ideas that were considered on top of the aim and objectives listed above:

Hypothesis 1

The inclusion of superplasticizer in a non-air entrained concrete affects the results of the spacing factor due to its side benefit of air entrainment. The possibility of validating a concrete's freeze-thaw performance based on the spacing factor is inert as no true value can be calculated with the development of new and improved superplasticizers.

Hypothesis 2

The addition of salt into the concrete designs was an attempt to understand whether the lightweight concrete had the ability to absorb the salt and prevent further ingress. With a high-water absorption value, the lightweight material would absorb a high quantity of saline solution, which would dry out in the aggregate leaving the salt crystal, and the same process would begin again creating a "salt defence" against ice infiltration.

Hypothesis 3

The densification of concrete during the carbonation process does not influence the durability of concrete during freeze-thaw. Non-air entrained samples are succumbed to severe cracking after a number of cycles, however, concretes which contain air entrainer are able to resist freeze-thaw with only minor scaling meaning that the air entrainer combined with the carbonated concrete create a protective film around the voids.

The densification of the concrete containing fly ash addition increases the possible strength of the sample but is also a consequence as with the reduction of void space reduces capacity for the ice to expand leading to cracking and eventual mass loss.

Hypothesis 4

Carbonation of concrete is a hindrance to the durability during freeze-thaw conditions for non-air entrained concrete when compared to non-carbonated. However, with the addition air entraining admixture, the air entraining admixture (AEA) appears to provide further protection when the *microbubbles interact with the carbonates resulting in the premise that with AEA, concrete has the ability to resist freeze-thaw conditions whether or not it was carbonated.*

1.5 Outline of Thesis

Chapter 2 is a review of current literature focusing on the freeze-thaw effects on different concrete types and understanding how the microstructural properties such as the spacing factor determine whether a concrete is capable of withstanding freeze-thaw attack. The review dates back to 1945 when Powers theorised the Spacing Factor used to determine a concretes resistance to freeze-thaw. The review further discusses current developments in technology which can quickly and accurately determine a concrete's microstructural properties in less time. Lastly, the literature review looks at the development of the European standards for concrete specification for freeze-thaw resistance.

Chapter 3 details the experimental programme for the project, the materials used, concrete mix proportions, fresh concrete properties and the test methodologies.

Understanding the influence of different cement types on the microstructural properties is presented in Chapter 4. Automated air void analysis is used for this chapter as the conventional method can take up to 6 hours to complete a sample whereas the automated method only takes 20 minutes. The range of air void characteristics such as the spacing factor, specific surface and the air content of hardened concrete are compared to establish a relationship between the parameters and how they are used to detail a concrete's future performance in freeze-thaw.

Freeze-thaw testing a range of different air and non-air entrained concretes was reviewed in Chapter 5. CEM I, CEM II/B-V, CEM III/A and CEM II/A-L concretes were tested under freeze-thaw conditions varying the strengths between 20-60 MPa (Series 1 and 2) to create a range of data for comparison during the project and with previous studies. The level of air content was also varied to understand the implications of over-entrainment in the concrete and investigate the physical characteristics and durability during freeze-thaw (Series 3). Moreover, the addition content was increased past the maximum allowance detailed in BS EN 197-1 to determine the possible benefits of further additions (Series 4). Other parameters were investigated including changing the aggregate type and the influence of admixture compatibility.

The influence of lightweight aggregates on freeze-thaw resistance is discussed in Chapter 6. Lightweight aggregate is a material which has been developed from fly ash to reduce the self-weight of a structure enabling more load to be taken before failure. The chapter looks at the microstructure of the aggregate identifying the characteristics such as porosity and pore size distribution which makes the material very good during freeze-thaw aside from the fact that the freeze-thaw testing of the aggregate itself is shown to be detrimental.

Chapter 7 outlines the development and update to the current freeze-thaw test method, CEN/TS 12390-9. Currently, the freeze-thaw test is shown to be too harsh regarding the UK climate and whilst it does provide security as to the concrete's performance during temperature changes, it does not show a realistic climate setting. This chapter looks to change the parameters of the test including the temperature profile, salt concentration, influence of carbonation on the freeze-thaw resistance properties and testing of the cast surface to determine a realistic result from the test method rather than testing the strongest section of the concrete.

Chapter 8 details the conclusions drawn from the research and identifies the practical implications of the work investigated. Recommendations for further studies are also given.

Chapter 2
Literature Review

2.1 Introduction

This chapter reviews the current published work into the research and experimentation of concrete durability, the specification of concrete for the use in structural application and the destructive implications of the freeze-thaw process on the hardened concrete. Analysis has been carried out on climate change that has been on going because of increased carbon dioxide (and others) emissions. Further analysis is done on the various sectors where carbon dioxide is produced in the UK and a closer inspection on the output of carbon dioxide produced during the production of concrete and how that has been reduced.

The review focuses on the effects of cementitious addition material on air entrainment properties and the freeze-thaw performance of the materials and further analysis of the current cement standards to determine whether they are suitable for freeze-thaw prone concrete. Previous studies (Fagerlund, 1995; Concrete Society, 1999) have been conducted looking at various parameters such as the cement type, design strength and air entrainment to understand the mechanisms which contribute to the deterioration of concrete.

In a bid to further understanding the microstructure of air entrained concrete, new technology has been implemented to analyse how the air void system and how varying sized pores help protect the concrete against deterioration. This technology helps in the process of analysing the pores and calculating the parameters such as spacing factor, specific surface and air void distribution which took far too long when done manually. Critical analysis will be conducted on the published work to determine its precedence and whether the studies conducted are plausible and can be used.

2.2 Impact of Climate Change on the Air Temperature

For about the past 100 years the Earth's surface temperature has increased by about 0.89°C due to global warming (The Met Office, 2015) meaning that extrapolation of the data leads to an ever increase in the Earth's surface temperature. This can be attributed to the increase in the carbon dioxide concentration due to emissions.

In the UK, climate change is of major concern with the temperatures fluctuating in such a way that the winters have become milder and wetter with the odd one being very harsh (The Met Office, 2017). Figure 2.1 describes the highest, lowest and average air temperatures for January from 1997 to 2017 for Dundee and Figure 2.2 for July during the same period. Dundee was chosen as this city sits on the coast open to the sea wind allowing fresh cool air to pass through. There are not a lot of tall structures in the city affecting the air temperature so they sea air will provide a continuous flow of cool air. The city sits just 18m above sea level and the temperatures were taken for this city at Dundee airport.

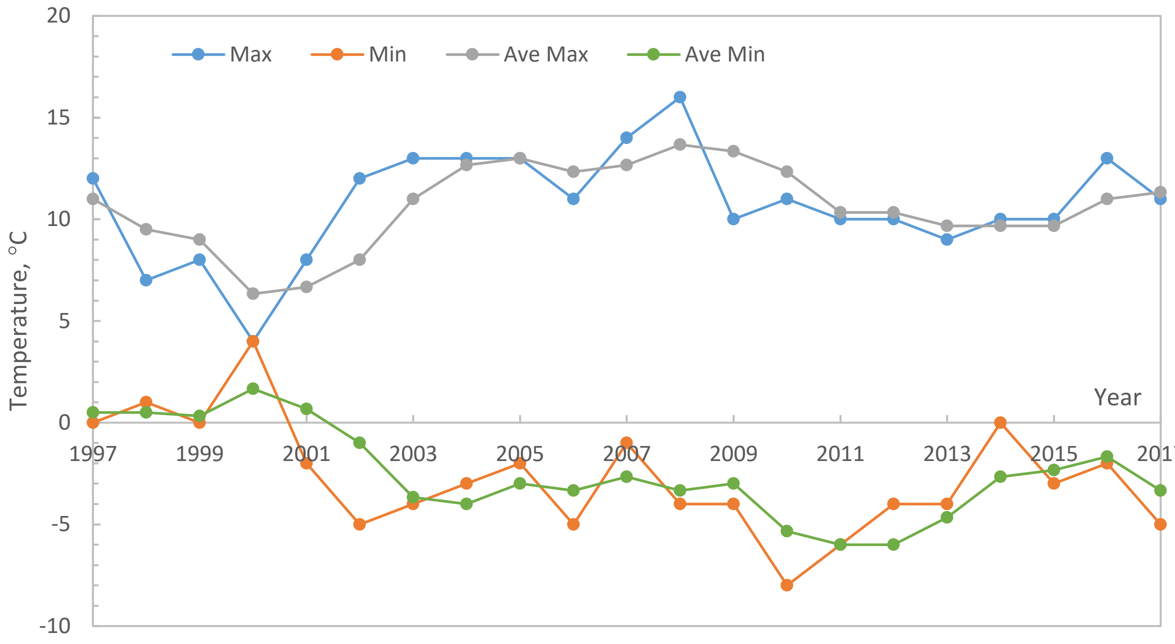


Figure 2.1 Highest and lowest air temperatures with moving averages for January (coldest month) from 1997 to 2017 for Dundee (The Met Office, 2017)

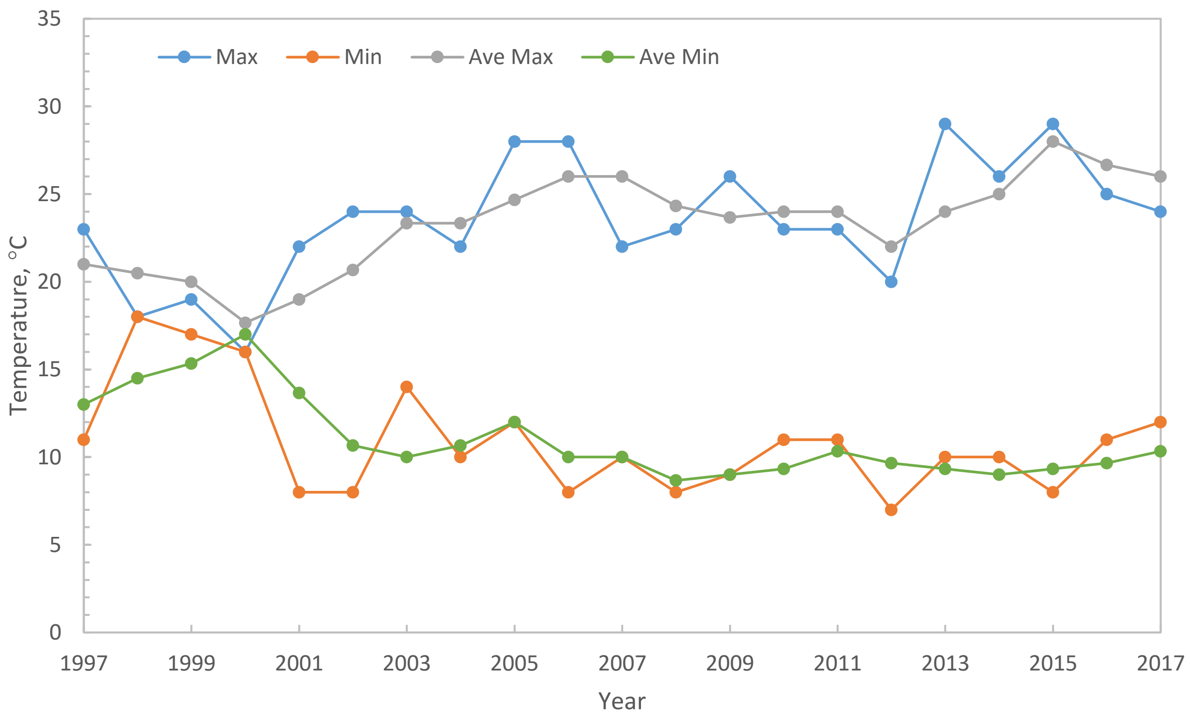


Figure 2.2 Highest and lowest air temperatures with moving averages for July (warmest month) from 1997 to 2017 for Dundee (The Met Office, 2017)

As shown, the lowest temperatures recorded for each year are below zero with several being very low (2002, 2006 and 2010) and others barely freezing (1999, 2007 and 2014). The highest recorded temperatures fluctuate considerable each year with temperatures ranging from 4°C to 16°C.

From Figure 2.1 and Figure 2.2, they illustrate that the temperature has fluctuated quite significantly for the past 20 years especially during the winter when temperatures reach below freezing. The temperature is seen to range from being 10°C (year 2010) one day and within the same month in the same year go down to -8°C. Temperature differences such as these show that it is hard to protect against environmental exposure, but ground temperatures however give a different reading.

In Figure 2.3 are the maximum and minimum air temperatures recorded in (a) January and (b) July for 2016 across various cities throughout the UK. As shown, the temperatures for January vary across the country ranging from being mild at 14°C in parts then dropping down to cold temperatures at -4°C. Though these temperatures are only readings taken from a certain point during the day on a single day, it still provides evidence that there are significant temperature fluctuations occurring. Although during the summer the temperatures are relatively similar across the country with temperatures ranging from the mid to late twenties down to early teens.

It is not just the UK which suffers from significant temperature fluctuation. Similar trends are occurring across Europe. Figure 2.4 illustrates large temperature differences during the winter months where the maximum and minimum temperatures described are for those during January 2016.

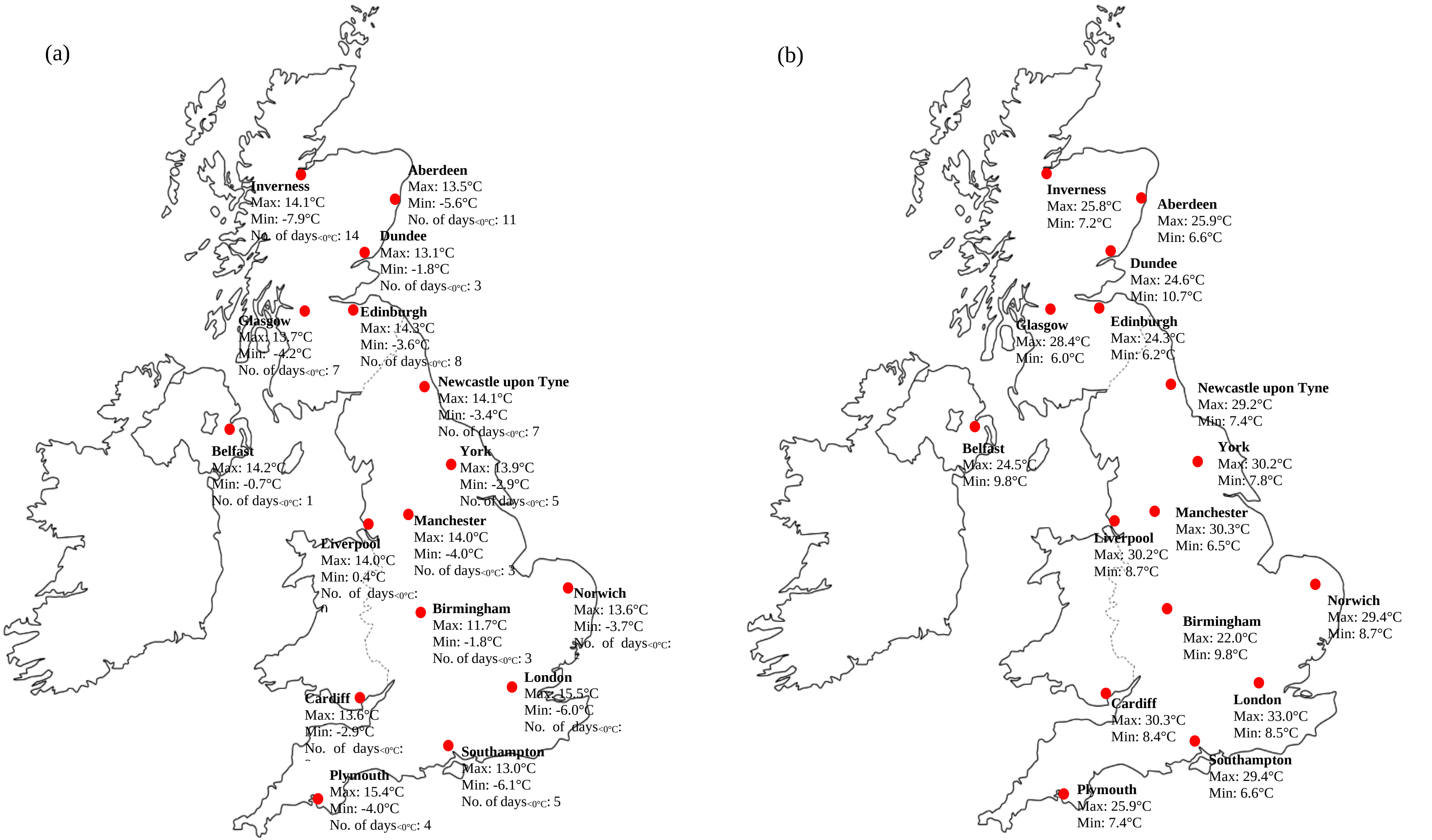


Figure 2.3 Maximum and minimum temperatures recorded for UK cities in 2016 for (a) January (coldest month) and (b) July (warmest month) and the number of days recorded where the temperature was below 0°C (No. of days$_{<0°C}$)

Figure 2.4 Maximum and minimum air temperatures recorded in January 2016 and the number of days where the temperature is below 0°C for a number of capital cities of European countries (T&D, 2017)

2.3 Concrete Design and Durability

With approximately £103bn turnover within the UK construction industry and the majority on the structures being concrete and steel structures, more focus is now placed upon the durability of concrete ensuring that it withstands environmental implications they are subjected to. This led to an annual repair cost of £550 million encouraging more research to be conducted. Furthermore, with the government projecting forecasts for the global construction industry market to grow by over 70% by 2025 and targets such as (HM Government, 2013):

- a 33% reduction in the initial start-up cost of construction and whole life costs;
- a 50% reduction in the overall time from design to construction completion;
- a 50% reduction in greenhouse gas emissions in the construction industry

To be reached it is now a necessity that research be conducted with regards to the durability so that reduction in the maintenance and repair cost are reduced.

2.3.1 Inhomogeneities in Concrete

Uniformity in the concrete has been well established as described by (Kreijger, 1990). Figure 2.5 illustrates the various layers that exist in the concrete. It is understood that the outermost concrete (or surface-crete) layer is to be the worst of the layers in comparison to the core and with this in mind it is a necessity that this layer be designed to counteract the everyday mechanical, chemical and physical attacks.

It was put forward by Kreijger (1990) that the outer layer of the concrete is divided into separate 'skins' as shown in Figure 2.5. These 'skins' comprise of two layers, the outermost being the cement skin which is approximately 1 to 3 µm thick and is comprised mainly of cement particles. This layer is generally observed around the rebar and coarse aggregate. Moving inward, a layer of mortar ranging from 1 to 5 mm thick divides the rich cement skin from the bulk concrete. The concrete skin is the last line of defence against foreign agents and the main cover for the bulk concrete (Kreijger, 1990).

Between the aggregate/rebar and the concrete skin lies the cement skin and with the cement skin is the interfacial transition zone (ITZ). The transition zone has two parts to it; A thin layer measuring approximately 1µm thick of products which form on the aggregate/rebar's surface which includes any reactions that may occur between the aggregate/rebar and the cement. The other part is much larger containing the aggregate particle which can affect the packing of the cement grains around the aggregate/rebar and possibly affect the microstructure on the ITZ (Scrivener & Pratt, 1996). Furthermore, the ITZ has a higher porosity than the rest of the concrete meaning that the surrounding paste is weaker and more susceptible to deterioration. However, lightweight aggregate produces a denser ITZ because of it porous surface (Neville & Brooks, 2010).

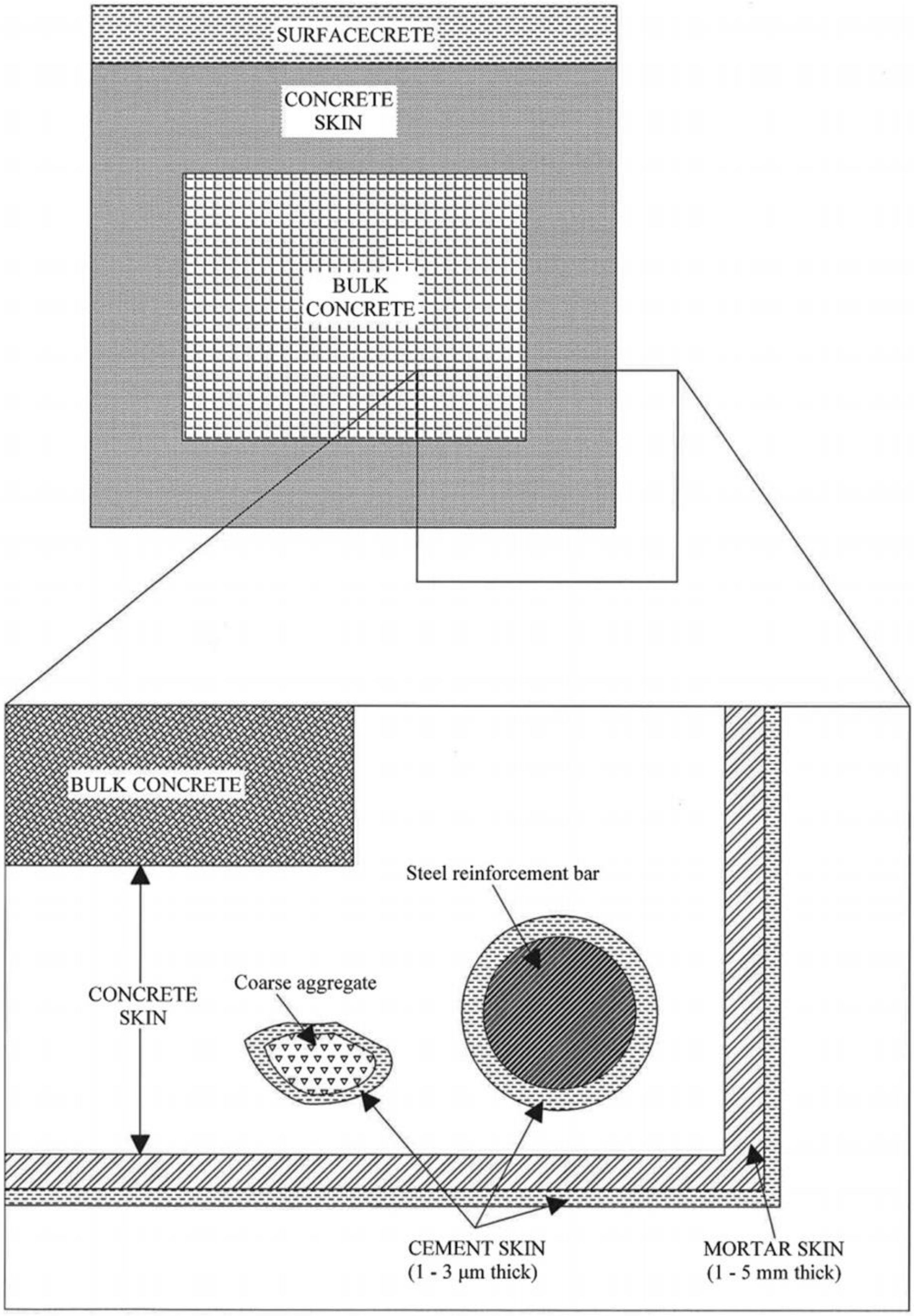


Figure 2.5 Non-uniformity throughout the concrete, depicting a skin effect on the outermost layers and the interfacial transition zone between the aggregate/reinforcement and the cement paste (Kreijger, 1990; Newlands, 2001)

2.3.2 Transportation Mechanisms in Concrete

Freeze-thaw deterioration is known to cause major problems in concrete and one of the main factors which aid in the deterioration is the transportation mechanisms involved in moving foreign agents and this aids in the degradation of the concrete by way of the steel reinforcement. The damage to the

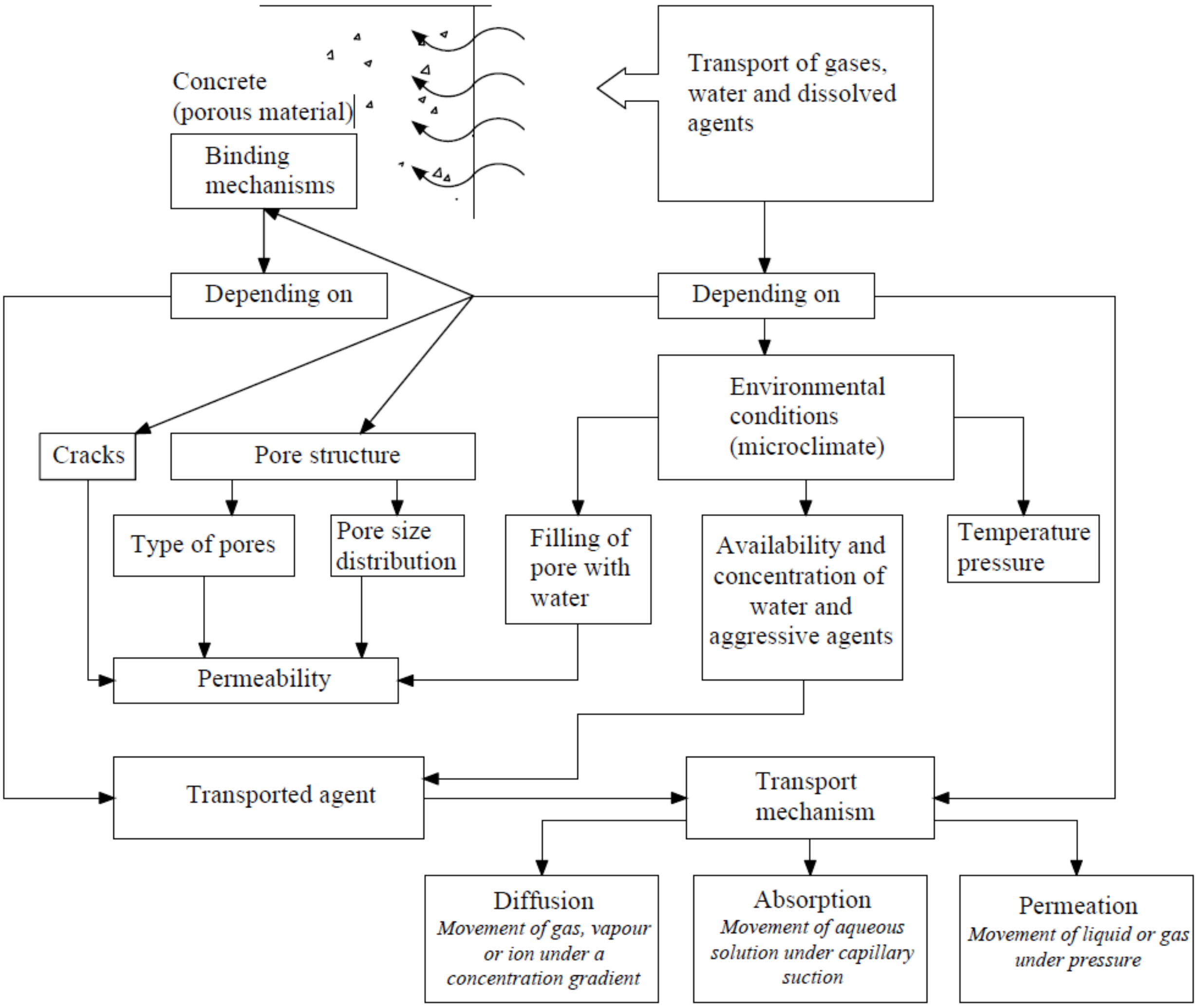


Figure 2.6 Diagrammatic representation of the interconnection between the micro-structural properties of concrete, the environmental conditions and transportation mechanisms (CEB, 1992; Newlands, 2001).

concrete is a result of the ingress of foreign agents through the cracks and pores (CEB, 1992). The ingress of the foreign agents is through three environmental factors and generally it is through either one or a combination of; diffusion, absorption and permeation.

Though, primarily, it is a combination of the three mechanisms which cause the ingress of foreign agents, but each one of the mechanisms works in a different manner and is also dependent on the various factors such as the micro-structural properties of the concrete and environmental factors. Figure 2.6 diagrammatically illustrates how the concrete properties are interdependent on the environmental conditions (CEB, 1992; Newlands, 2001).

2.4 Freeze-Thaw Durability of Concrete

Freeze-Thaw attack has been discussed and tested and whilst the idea has been there, determining what mechanisms have been causing the damage has become a difficult task. Concrete has been subjected to freeze-thaw attack for decades, but it was not until Powers (1945) who devised the first theory which was later expanded on and led to the cultivation many different theories being developed to explain the mechanism behind freeze-thaw attack. Table 2.1 List of freeze-thaw definitionsoutlines the definitions used in this research project.

Freeze-thaw attack is not just simply deterioration of concrete by ice, there are many different mechanisms that have been theorized and are divided into two categories (Figure 2.7):

- Internal freeze-thaw damage relates to deterioration of the concrete within the sample and is more problematic of the two and this will affect the concrete's integrity;
- Freeze- thaw salt scaling is the loss material on the surface of the concrete and is more related to the aesthetics of the concrete, however internal damage does occur with continuous cycles.

Table 2.1 List of freeze-thaw definitions used during this study

Phrase	**Definition**
Freeze-thaw mechanisms	This defines the many mechanisms (both internal freeze-thaw and freeze-thaw salt scaling) which try to explain why the phenomena occurs and what causes it.
Freeze-thaw attack	Defined as when the phenomena attacks or begins to deteriorate the concrete, internally and externally.
Freeze-thaw damage	This relates to the damage that is left once freeze-thaw attack/cycling has taken place and the concrete moisture is reduced enough to prevent further attack.
Freeze-thaw durability	The term used to describe a concrete's ability to withstand freeze-thaw attack and its prevention from damage.

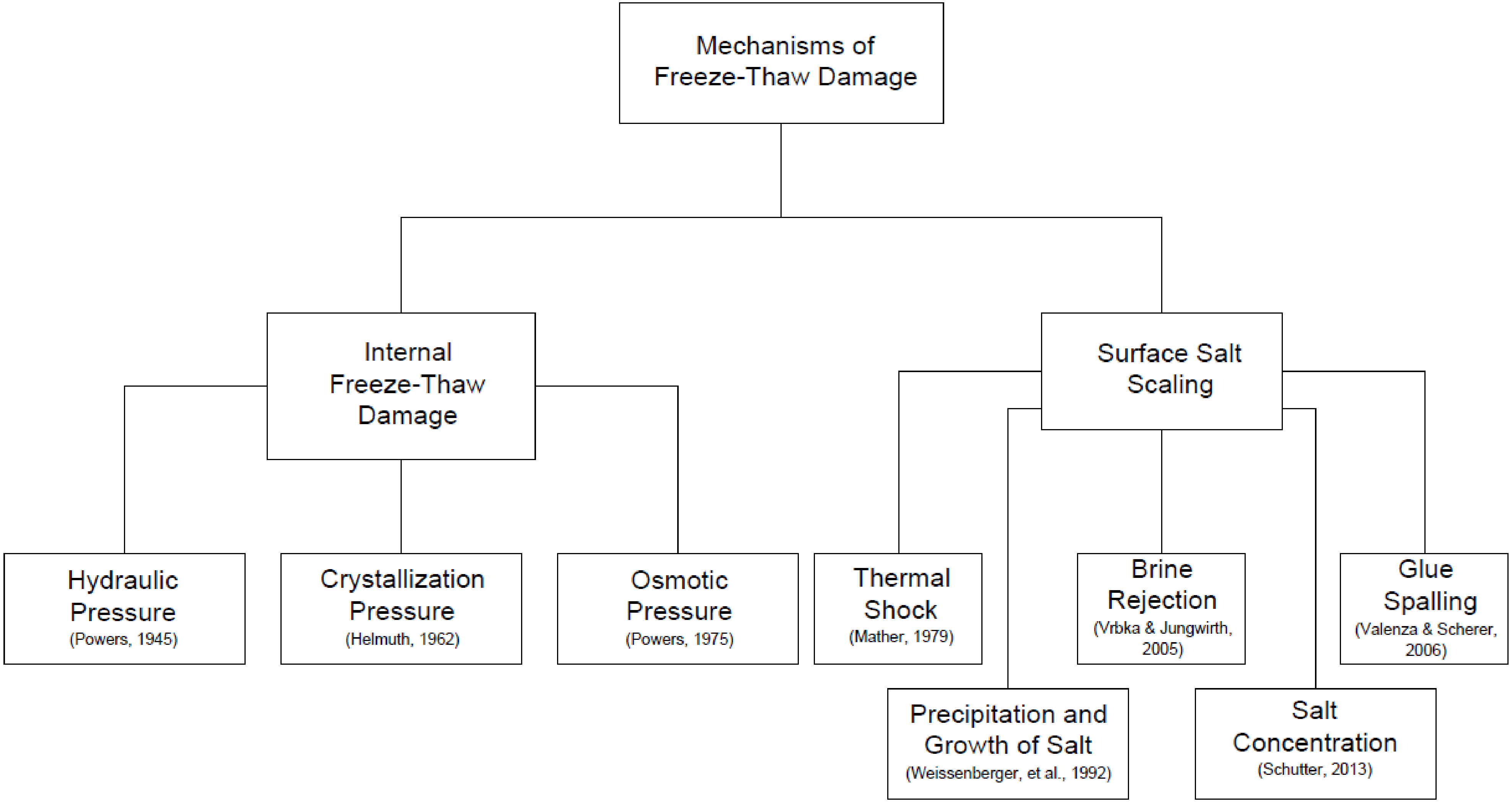


Figure 2.7 Flowchart showing the different internal freeze-thaw and salt scaling damage mechanisms and the author of the theory

2.4.1 Mechanisms of Internal Freeze-Thaw Damage

It has been identified that internal factors which influence the damage caused by freeze-thaw (CIRIA, 2001) are due to the size and spacing of the pores in the cement paste. From this, the complete saturation of these pores has been considered to be the main cause of the damage during a cycle of freeze-thaw. During this process water enters the specimen whereby the pores begin to fill with water (Schutter 2013, Dyer 2014). When the pores fill with water along with a drop in the temperature, it solidifies the water to ice. Consequently, the continual freezing of the water to ice will result in a constant increase in the expansion and therefore the ice will apply pressure to the internal pore wall (Schutter 2013, Shang & Yi 2013).

As each cycle does a full rotation then more and more water enters the cracks and the pores. The cracks increase in numbers and size until the eventual scaling, spalling or, under extreme circumstances, collapse (Diao, et al. 2013, Schutter 2013). Further mechanisms such as salt scaling have been identified to have serious effects on the concrete once cracks are visible. In countries where the climates are mainly cold, namely the UK, the use of de-icing salts on the roads and pavements to melt the snow/ice is widely used. However, the use of this material has caused significant damage to the concrete surface (Valenza & Scherer, 2006).

<u>Theories of Internal Freeze-Thaw Damage</u>

Over the years many theories have been established to explain the cause of internal freeze-thaw damage and whilst there is no conclusive answer, prominent theories have shown to describe the likely causes of the damage. It has been considered extensively that freeze-thaw is a major cause of concrete deterioration and so a high volume of research is focused in this field. Table 2.2 describes what the mechanism is, who theorized the mechanism, cause of the mechanism, an explanation of the deterioration for each theory suggested for internal freeze-thaw damage along with advantages and disadvantages of each mechanism.

Table 2.2 List of internal freeze/thaw damage theories detailing the mechanism, the cause of the mechanism and advantages and disadvantages for each mechanism

Mechanism	Theorized by	Cause of mechanism	Explanation for Deterioration	Advantages	Disadvantages
Hydraulic Pressure	Powers (1945)	The pressures associated with the expansion of ice during the decrease in temperature and the *apparent* saturation of the concrete.	- Ice expands up to 9% of its volume and has the capability to withstand pressures up to 200 MPa (Dorsey, 1940). - Theory explains that water begins to freeze in the capillary pores. - *Fully saturated* capillaries cannot accommodate the expansion of ice so the pore must dilate or lead to the expulsion of water. - This expulsion produces pressures exerted on the pore wall.	- Simple explanation on how the concrete deteriorates due to pressure from expanding ice. - Reducing the internal pore sizes would help increase the rate of freezing.	- Does not explain other phenomena that occur during the freezing process. - Defining a *fully saturated pore* is difficult because there is no method to determine full saturation meaning that this definition is unfounded.
Crystallization Pressure	Helmuth (1962)	Crystallization pressure is a result of salt crystal growth in the pores from a supersaturated solution that exert stress on the pore walls (Scherer, 1999).	- Salt crystal growth in one pore is not enough to cause cracks to form. - Instead an accumulation for stresses with a large enough region would increase the risk of propagating out with the concrete's pores. - Higher damage percentage is seen to occur in the smaller voids, even though the formation of the crystals begins in the larger voids. - Figure 2.8 Graph depicting freezing point of various void sizes both entrained and entrapped showing freezing points of various void sizes.	- The mechanism details salt exerting a force on the pore walls rather than ice. - Follows the idea that a solution, which is more than saturated, deposits salt in the pores which then crystallizes and applied pressure to the void wall.	- Mechanism has been investigated for years by many researchers (Everett, 1961; Hansen, 1963; Beaudoin & MacInnis, 1974) and still unable to use as a viable theory. - Though defined as an internal damage theory it seems to act more like a salt scaling theory.
Osmotic Pressure	Powers (1975)	An approach to explaining the continuous growth of ice inside the concrete pores when the temperature remains below 0°C (Ronning, 2001).	- Minimum pressure required to prevent the inward flow of the pure saline solution across a semipermeable membrane. - The semipermeable membrane allows the pure solvent to pass through but not the salt molecules. - This stabilization of the salt concentration of each side defines osmosis	- Explains why the flow of water moves towards the larger voids from the smaller voids. - The theory is a follow on from the hydraulic pressure theory by Powers which covers more phenomena.	- Though theorized that this mechanism causes damage by itself, another mechanism is required to deteriorate the concrete. - The addition of another mechanism, in this case crystallization pressure, is still not enough to meet the criteria for the freeze-thaw mechanism.

	- This mechanism has been seen to work with another mechanism, mainly crystallization pressure as identified by Valenza & Scherer (2007b).	

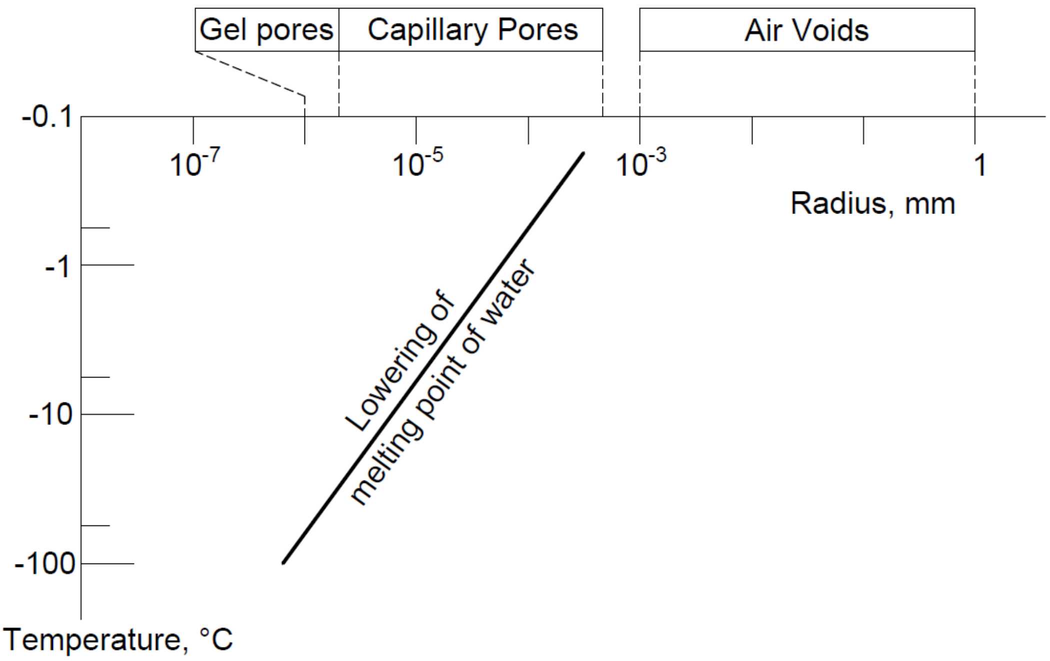


Figure 2.8 Graph depicting freezing point of various void sizes both entrained and entrapped (Harnik, et al., 1978)

2.4.2 Mechanisms of Freeze-Thaw Salt Scaling

As previously stated, internal freeze-thaw by itself is not the only cause of damage to the concrete surface. Working in tandem with freeze-thaw attack the effects of de-icing salts on the concrete have caused salt scaling (Figure 2.9) as described by Schutter (2013). Though this area of research is such a wide field, there is no definitive explanation why this type of damage occurs, consequently, this means that there is no identifiable solution to the deterioration.

Figure 2.9 Comparison between concrete pavements, before and after salt scaling (Valenza & Scherer, 2007b)

Valenza & Scherer, (2007a) compiled experimental data about the phenomenon and details the characteristics of salt scaling and the factors which have influenced the damage. Valenza & Scherer (2007a) explain that although salt scaling has no effects on the internal mechanics of the concrete specimen, only surface scaling, it can however lead to long term damage whereby moisture can infiltrate the exposed surface and affect the overall durability of the specimen especially if the concrete has steel reinforcement.

One revelation which was discovered from the studies was that freeze-thaw attack on its own is known to damage the concrete internally leading to spalling of the material surface. Though what has seemed to surprised researchers is that with the application of salt on the concrete surface, it has shown to reduce the build-up of internal frost in the voids of the specimen. This then leads onto the query whether it is the freeze-thaw attack itself which is causing the scaling and not the application of salt (Valenza & Scherer, 2007a).

Earlier in the report Valenza & Scherer (2007a) quickly dismissed work done by Klieger (1956) saying that the results were misleading the reader. Though later on the statement they made detailing that perhaps scaling is the result of freeze-thaw attack, by the intrusion of water only, seems to be a contradiction but raises an interesting point whether it is more effective to have salt mixed in with the concrete design.

Following this research another paper produced by Copurglu & Schlangen (2008) stated that one of the main cement mixtures (GGBS based cements) are the area of focus for freeze-thaw and salt scaling attacks. They looked at the work done by Valenza & Scherer (2006) and concluded that based on the theory of glue spalling, determined that the stresses are due to the shrinkage of the ice, detailing there are three possible consequences for this; thermal shock, growth of salt and salt concentration are the main focuses for the research into salt scaling.

Theories of Salt Scaling Damage

Similarly, to internal freeze-thaw damage, salt scaling has been extensive researched to try and determine the cause of the concrete damage. Over the years many theories have been considered and justified, and many of the theories are valid. There are three main theories with the addition of another two mechanisms recently considered and investigated (Table 2.3).

Table 2.3 List of internal freeze/thaw damage theories detailing the mechanism, the cause of the mechanism and advantages and disadvantages for each mechanism

Mechanism	**Theorized by**	**Cause of mechanism**	**Explanation for Deterioration**	**Advantages**	**Disadvantages**
Thermal Shock	Mather (1979)	Thermal shock takes place when there is a sudden change in temperature due to the ice on the surface melting because of the latent heat from the concrete specimen.	- This occurs because when ice is subjected to a saline solution the melting point of ice reduced. - Since the melting point of the ice is reduced, the heat required to melt the ice is taken from the exothermic reaction in the concrete mixture.	- Explains why the sudden appearance of cracks on the surface. Similar idea to putting ice cubes into warm water the sudden cracks that appear.	- Not suitable for laboratory conditions. A pre-mixed saline solution is used on the concrete meaning that the results do not give a true representation of the real world.
Precipitation and Growth of Salt	Weissenberger, et al. (1992)	The formation of ice from a saline solution the crystal lattice which forms does not consider the salt ions in the solution. The salt ions form a series of branches rather than being incorporated into the ice lattice. This then leads an increase in the solution’s concentration.	- Since the temperature is below the minimum, it is shown that there is not enough salt present in the solution. - Also, the temperature is not low enough for there to be significant damage to be inflicted on the concrete. - The concentration of NaCl solution will equate to that of the concentration of the solution applied to the concrete surface, for example rainfall or sea water. - These specimens are out in the field and are subjected to the saline solution drying. When this occurs, the salt in the solution will increase and cause precipitation of the salt leading to damage of the concrete.	- Salt ions branching and expanding in the concrete then applying pressure to the pore walls does explain damage. - Mechanism takes time to damage concrete as it requires constant applications of de-icing salt.	- During the summer months the built-up salt branches would be washed out due to the high volume of summer rain (especially in the UK).

Table 2.3 (contd) List of internal freeze/thaw damage theories detailing the mechanism, the cause of the mechanism and advantages and disadvantages for each mechanism

Mechanism	Theorized by	Cause of mechanism	Explanation for Deterioration	Advantages	Disadvantages
Salt Concentration	Schutter (2013)	Continuous applications of de-icing salt decreases the freezing point for different layers of the concrete.	- Continuous layers of de-icing salt lead to an increase in the salt concentration. - Freezing temperature lower further into the concrete due to less salt. - Top layer and inward layer of concrete are subjected to freezing but an intermediate layer remains unfrozen due to salt solution. - When temperature drops further solution is liable to freeze causing hydraulic pressure on the top layer forcing it off, hence scaling damage.	- With multiple layers of salt used on roads and pavements, this theory would explain the scaling on concrete surfaces.	- This mechanism seems to only work in conjunction with another mechanism i.e. hydraulic pressure. - Salt solution being pushed against the top layer would not push the concrete off, the salt would melt the ice before damaging the concrete.
Brine Rejection	Vrbka & Jungwirth (2005)	Decrease in the temperature causes the inorganic salt to be expelled from the salt solution. After a certain period, the frozen solution will deform on the surface causing stresses on the concrete.	- Inorganic salt (such as NaCl) in a saltwater solution is frozen and the salt particles are pushed or rejected out of the solution towards unfrozen solution. - Brine expelled out of the ice layer has a higher salt concentration in the unfrozen water. - With the brine being rejected, density of water increases in direct proportion to the salt concentration.	- The expulsion of the organic leaves water in the pores of the concrete meaning that not only would surface scaling take place but internal freeze-thaw damage could occur.	- If the brine is being rejected from the concrete to the surface then surely the build-up of salt would prevent any ice formation.
Glue Spalling	Valenza & Scherer (2006)	Ice sticks to the concrete surface and when the temperature drops, the ice contracts and pulls the concrete off the element.	- Rough concrete surface allows water to pond. The water then freezes sticking to the concrete and contracting as temperature drops. - As this happens, tensile forces begin to form with the eventual fracture occurring in the ice taken the same shape as the fractures in the concrete (Figure 2.10).	- If the surface is wet or rough then ice would easily stick to it.	- For the ice to scale the material, there would need to be cracks in the surface so that the ice could pull out the concrete.

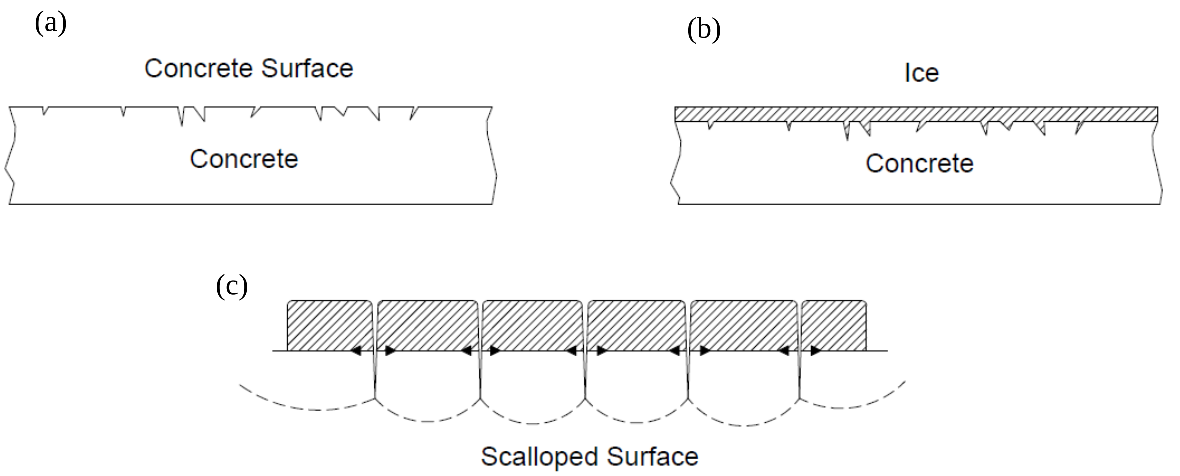


Figure 2.10 Process for glue spalling (a) concrete surface before ice formation,; (b) concrete surface after ice formation and; (c) ice contracting pulling the concrete away from the surface and causing it to shear (Valenza & Scherer, 2006)

2.4.3 Factors Influencing Freeze-Thaw Damage of Concrete

In the previous section, the mechanisms for internal freeze-thaw and freeze-thaw salt scaling were discussed detailing many different mechanisms that contribute to freeze-thaw damage. However, the damage caused by these mechanisms does not fully explain why the deterioration occurs. Hence, there are also external factors which influencing the deterioration.

2.4.3.1 Degree of Saturation of Concrete

One of many factors which must be considered when identifying the influencing factors is the degree of saturation in a concrete specimen. For concrete, the degree of saturation is determined by the volume of free water which is currently available in the pores (Schutter, 2013). Apparently, when a *dry* sample undergoes freeze-thaw there will be no damage as there is no moisture in the concrete specimen. The idea that a sample is dry is not entirely true. There is no way to tell where a sample is completely dry especially in the real world so that statement is redundant. Mehta & Monteiro (2006) suggests that there is a critical degree of saturation where the concrete will experience cracking or spalling of material at even low temperatures.

Moreover, it has been recognized that the difference between the critical degree and the actual degrees of saturation that actually determines the resistance against freeze-thaw attack (Mehta & Monteiro, 2006). The deterioration mechanisms can be pinpointed to the limit for the volume of the water content which cause the concrete damage. This is defined by the critical degree of saturation (CEB, 1992). The degree of saturation is based upon several parameters such as the pore size distribution, the age of the concrete, external factors which influence the rate of the freeze-thaw cycle and the moisture content between each cycle. These factors influence the deterioration of the concrete and cause the concrete to be susceptible to the deterioration mechanisms (CEB, 1992).

Fagerland (1975) suggested that when the degree is below that of the critical, there is not observed damage occurring to the concrete. However, if the degree of saturation were to exceed the critical degree then damage would occur. Using this theory of critical degree, a new method (S_{cr} method) was considered to assess freeze-thaw durability of concrete (Fagerland, 1977).

The method entails determining the critical degree of saturation by testing sealed specimens with varying amounts of water to freeze-thaw cycles. Another set of specimens are measured by their ability to absorb water identifying a *potential degree of saturation*. This is reached during very moist conditions (Fagerland, 1977). It is known as the capillary degree of saturation (S_{cap}) which then can be used to determine the freeze-thaw resistance, F:

$$F = S_{cr} - S_{cap} \qquad 0.1$$

The critical degree of saturation is technically independent of the environmental conditions whereas the capillary degree of saturation is solely dependent on the external conditions as it relates to the absorption of water. Therefore, F tends to translate into potential freeze-thaw resistance of various concrete types for different environmental conditions.

2.4.3.2 Concrete Mix Design Parameters

During the designing stage of a concrete mix there are many parameters which must be considered when designing a suitable mix: cement and water contents, the types of aggregate used, cement type etc. When concrete is in the preliminary stages of design, reducing the water/cement ratio would reduce the permeability, thus, increasing the hydraulic pressure. As a result, the water would struggle to move through the pores. However, there is conflicting statements as to whether a reduction in the permeability would increase the durability. Schutter (2013) identified that whilst in theory a reduction in the permeability would increase the pressures inside the concrete, in reality, the decrease in the permeability would make it difficult for the critical degree to be achieved and with a lesser volume of pores available for water to infiltrate and freeze.

Various cement types are available to use in concrete and whilst it provides better sustainability, there are draw backs to using these materials. As previous stated, CEM II/B-V is difficult to entrain as majority of the admixture is absorbed by the unburnt carbon (CIRIA, 2001). A reduction in the air entrainer means there is a reduction in the available air content, causing concrete to be susceptible to freeze-thaw attack. On the other hand, when the target air content is reached the compressive strength tends to be less than the design strength. Since majority of fly ash particles lie in the silt range (Sear, 2001), CEM II/B-V is prone to surface heave from freeze-thaw attack.

All concrete mixes use some form of aggregates whether they be fine, coarse or both. Generally, when concrete is produced for everyday use, local materials are used. When concrete is designed for specific durability, BS EN 206 and BS 8500 specify requirements for the concrete.

According to BS 8500, the aggregates used for both XF3 and XF4 conditions require the aggregates to be freeze-thaw resistant, especially XF4. This means that the aggregates must pass the magnesium sulphate (MS) test where only a certain mass of material can be lost during the test. For XF3 the maximum percentage of the total mass loss cannot be any more than 25% (MS_{25}) and for XF4, 18% (MS_{18}). Aggregates such as basalt and granite would be used for XF4 conditions.

Porous aggregate within concrete is considered to be a closed container meaning that when water moves quickly through the aggregate but not the cement paste this increases the probability that the water in the aggregate will freeze (Powers, 1956). For this to occur, the aggregate would need to be saturated by 90% and if this does happen then not only will the aggregate be damaged but so will the surrounding paste (Powers, 1956; Neville, 2011). This type of damage is known as D-cracking. Such aggregates include basalt and granite otherwise if plain local gravel is used then the aggregates are subjected to D-cracking. D-cracking is commonly seen on the surface and edges and joints of slabs, ones that are typically used for pavements (Dyer, 2014).

The use of lightweight aggregates (LWA) in concrete has cropped up in different projects and whilst there are benefits to using LWA in construction, laboratory experiments have shown to have mixed results when LWA is tested for freeze-thaw (Zaharieva, et al., 2004; Polat, et al., 2010; Shang, et al., 2014). BS 8500 details the use of LWA concrete for freeze-thaw conditions stating that this type of concrete can withstand extreme conditions. Polat, et al. (2010) looked at the effects of pumice and expanded perlite (replacing fine aggregates) on freeze-thaw resistance. Replacing 10% of the standard fine aggregate with LWA increased the durability due to the air voids acting like air entrainer. However, increasing the quantity of these aggregates to 20% and 30% would adversely affect the compressive strength and performance of the concrete.

2.5 Protecting Concrete Against Freeze-Thaw Attack

2.5.1 Air Entrainment in Concrete

Air entrainment is a process whereby air is purposely introduced into the concrete in the form of micro air bubbles which are distributed throughout the concrete and the result is a series of air voids which protect and prevent the concrete from deterioration when freeze-thaw attack occurs.

As previously stated, air is purposely introduced into the concrete. The entraining admixture is added during the mixing process allowing the formation of the bubble structure to be mixed in with the concrete (Goguen, 2012). This is known as air entrainment and not to be confused with entrapped air which is defined as air that is accidently trapped in the concrete during mixing and placement and must be removed via vibrating.

Ideally, the entrained air voids would be of the same size and uniformly distributed throughout the concrete, though in reality this is not the case (Figure 2.11). Bubbles are found to be of different sizes and the distribution do not have equally uniform spacing meaning that with both of these factors, the concrete has the possibility of having a decrease in the strength (Cordon, 1946; Elsen, 2001; British Standards Institution, 2005).

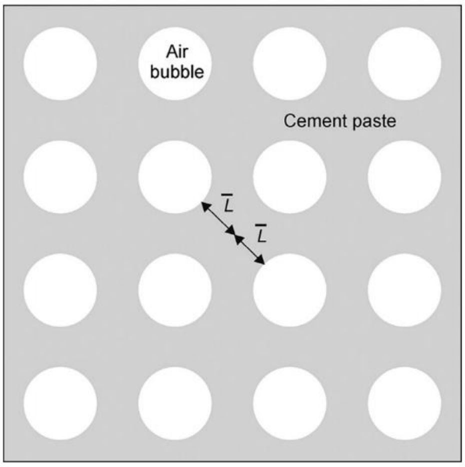


Figure 2.11 Idealized representation of uniformly distributed entrained air voids and spacing factor (L) in 2-D (Gagne, 2016)

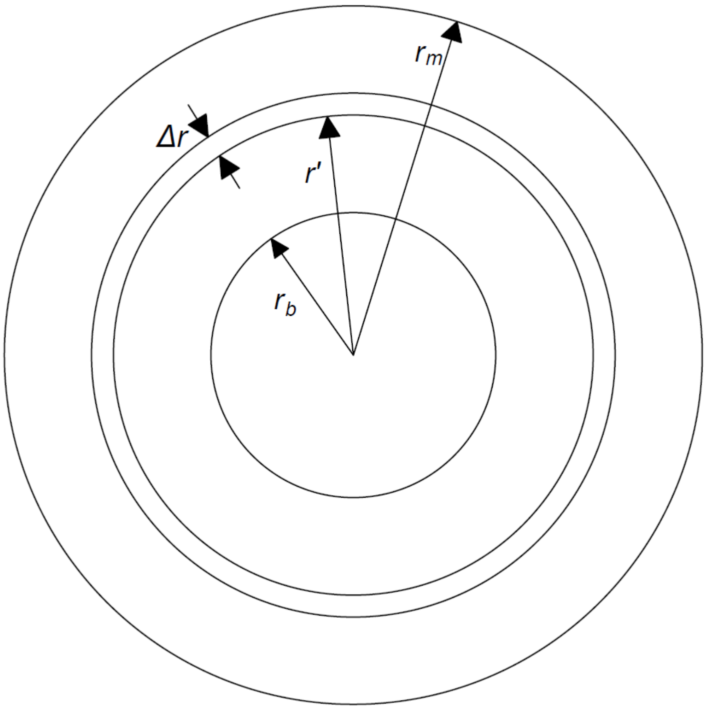
Air entrainment provides good protection against damage. Although full protection cannot be guaranteed, it still much better protection in comparison to concrete which is not air entrained (Mehta & Monteiro, 2006). However, when using air entrainment in concrete the cement content must be adjusted to compensate for the strength loss when using AEA. When AEA is used for every 1% of air content added, approximately 5.5 MPa of strength is lost so to counter this the cement content is increased to keep the strength the same as non-air entrained concrete (Wright, 1953; Schutter, 2013; Dyer, 2014).

Concretes such as CEM II/B-V, CEM III/A and now CEM II/A-L using limestone as replacment are the norm for concrete design. However, air entraining agents have not managed to 'keep up' with the constant development of different cements so the technology has not adapted. In other words, concretes like CEM II/B-V are very common in the UK but the ability to entrain air is difficult whilst trying to maintain the target strength. Pedersen, et al. (2008) explain that fly ash containing concretes have higher admixture demands, especially if there is fly ash containing unburnt carbon. Bearing that in mind, if the same amount of admixture is used as with CEM I there would be a reduction in the air content. On the plus side there are notable increases in strength of CEM II/B-V concretes at 90 days compared to CEM I due to the absorption of the admixture (Baltrus & LaCount, 2001; Peng, et al., 2007; Pedersen, et al., 2008).

Air entrainment of CEM III/A is understood to have little effect on the freeze-thaw resistance (Bijen, 1996) however, similar to CEM I and CEM II/B-V there is a reduction in the compressive strength compared to concretes that are non-air entrained (Wawrzenczyk, et al., 2016). Comparing CEM II/A-L to CEM I, the compressive strength loss is noted to be only slight (approximately 5% loss) with the addition of limestone (Githachuri & Alexander, 2013). The effects of entrainment on the strength of limestone concrete are similar to that of CEM I as limestone is classed as chemically inert then the strength loss is governed by CEM I (Neville, 2011).

2.5.2 Air Void Structure

The structure of the air voids in the concrete, whether they be entrained or entrapped, is an important factor which needs to be considered when concrete is subjected to freeze-thaw attack. Powers (1949) identified that it was not simply just an air void by itself but in fact there was a 'sphere of influence' that had to be considered. The void (Figure 2.12) is formed by several layers starting with the air void itself (r_b). Δr is the shield thickness surrounding the air void measured at a distance r'. The sphere of influence (r_m) is the boundary condition where the influence of the air void ends.



r_b – Radius of the bubble/air void

r' – Distance from particular element to the centre

r_m – Radius of sphere of influence

Δr – Shield thickness

Figure 2.12 Cross-section through air void depicting the various layers that make up the sphere of influence (Powers, 1949)

Some paste resides within the sphere of influence contain capillary pores that are filled with freezable water. As the temperature drops, the water within these pores freezes, which means that water unfrozen in the pores will be forced out to make room for the expanding ice. When this occurs one of two things are going to happen either, the concrete is going to expand along with the expanding ice and therefore liable to fracture or the unfrozen water will be expelled out the concrete or into a free air void (Powers, 1949).

2.5.3 Mechanism of Air Entrainment

There are many different mechanisms which cause internal frost damage and salt scaling and whilst the prominent mechanism has not yet been identified and addressed, many theories have been developed to explain the problem. That may be all well and good, but the situation stands as how does freeze-thaw damage remain manageable in the meantime? There are currently two methods in use to significantly reduce the damage caused by freeze-thaw attack; one method is to increase the strength of the concrete whilst the other is to use air entraining admixtures. The latter of the two is the preferred option as it minimizes the cost of concrete production.

The definition of air entrainment is the intentional implementation of air bubbles into the concrete mixture. In a perfect world, the bubbles generated in the concrete would be all the same diameter and have equal distribution through the structure, however, this is not the case, and the problem with the entrainment of air was that the bubbles in the structure were not evenly distributed and not of the same size. Much work that has been carried out already has confirmed that the range in bubble's diameter are very wide as described by Ley, et al. (2009).

As explained earlier, Powers (1945) established a spacing factor (an estimation of the longest distance to an air void) of 250µm (Hasholt, 2014) which was then reduced to 200µm (Backstrom, et al., 1958). A follow-on paper by Powers & Helmuth (1953) details experiments that showed that the pores (or air voids) can be classified into three groups. First being what Powers & Helmuth (1953) classed as cement gel pores which are very small spheres that are joined together chemically, as though as they were spot welded (Figure 2.13). From the figure, the black spots are detailed as the gel pores. This group of pores are known to freeze under typical freezing conditions.

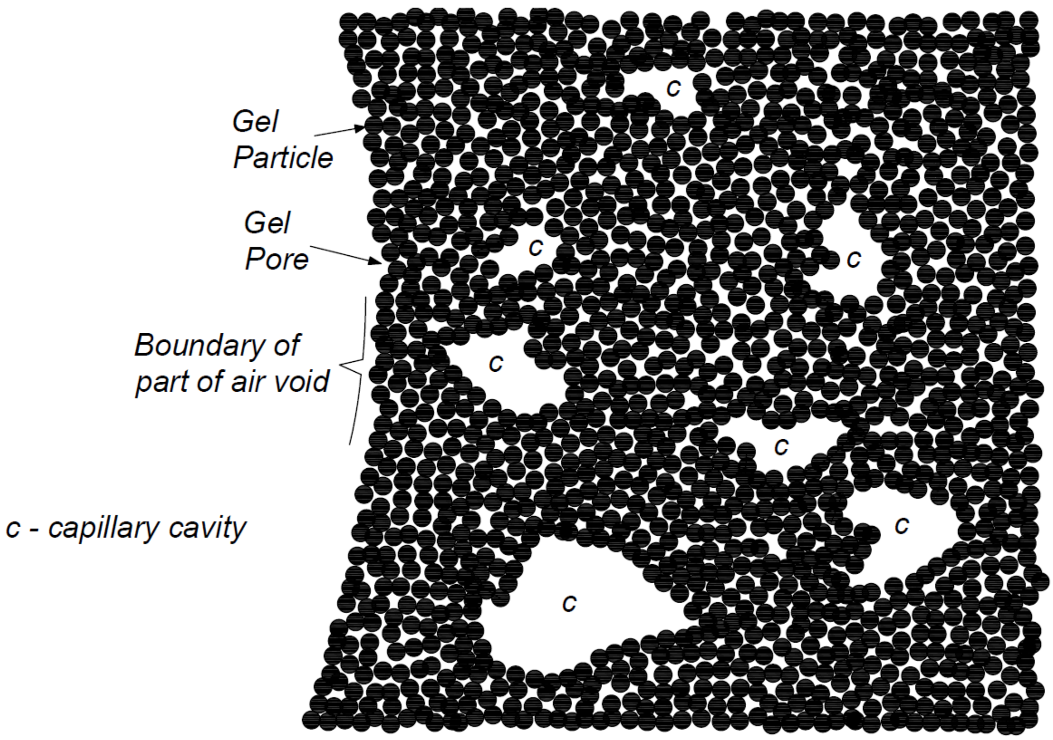


Figure 2.13 Diagrammatic representation of a paste structure (Powers & Helmuth, 1953)

The second class of pores are the capillary pores, which are the remains of the water filled pores in the fresh concrete and are much larger than the gel pores. The capillary pores have been observed to be sharing borders with the gel pores which allows the water to follow through whenever there is a change in the temperature (Chatterji, 2003). Because of the size of the pores, the freezing temperature is lowered meaning that as the size of the capillary pore is reduced in size, the freezing temperature is lowered too as a direct consequence.

The third class of air void is those that are purposely entrained into the concrete by mean of air entrainment. These types of pores are meant to be empty as these are used during the freezing conditions when water in the capillary pores freezes and expands resulting in the unfrozen water being pushed into the entrained voids, preventing in the deterioration. Although not mentioned, another class of air voids can be included. These are the entrapped air voids which are the unintentional entrainment of air. Though not purposely included in the concrete, these types of air voids still exist since it is very difficult to remove all trapped air in the concrete through vibration. In 1995, Neville describes that a typical bubble which is purposely entrained generally has a diameter of 50μm, whereas, bubble which have been accidentally entrapped have diameters which are significantly larger.

2.5.4 Factors Influencing Air Entrainment

A key point that has been made in several papers is the factors which influence the bubble (or air void) formation. The total air content was only able to be measured when the concrete was in the fresh state, and even though the results produced from the studies done (Shang & Yi, 2013; Liu & Hansen, 2015) show good results in terms of air content, once the concrete has hardened this has seen to reduce meaning that there are factors affecting the air entrainment.

2.5.4.1 Effects of Cementitious Materials

<u>Influence of CEM I</u>

The main cement type used in the concreting industry is of course CEM I or CEM I. This material has been used for centuries dating back to the middle ages. Cement is manufactured from a range of materials. These materials include calcareous materials like limestone or chalk with argillaceous materials like alumina and silica from clay and shale. Also, Marl, which is a combination of calcareous and argillaceous materials are added to the mix (Neville, 2011). Typical composition of CEM I is shown in Table 2.4.

CEM I is generally the simplest cement type to use when entraining as most of the admixtures are specifically designed for this cement type though an allowance for other cementitious materials have been considered when the admixtures are designed. CEM I has the capacity to entrain air in its structure without the air escaping, because the small air voids do not have the capability to abscond from the bulk paste phase as their buoyancy force is reduced (Du & Folliard, 2005).

Table 2.4 Constituents in CEM I (BSi, 2011a)

Constituent	Minimum (%)	Maximum (%)
CaO	60	66
Silica	18	25
Alumina	3	10
Iron Oxide	2	5
Water and Carbonic Anhydride	1	3
Magnesia	0.5	4
Sulphuric Anhydride	0.5	2.75

Preventing air voids from escaping during the casting process is a major advantage of CEM I. The viscosity of the paste coupled with the diameter of the entrained air voids determines how fast the air voids rise to the surface of the paste which is calculated using Stokes' law. If a high viscosity is to be used, then this is an increase in the thickness which acts as a 'cushion' that allows the concrete to hold the bubbles in place and can withstand any agitation that may occur. Moreover, with an increase in the viscosity, there is a reduction in bubble coalescence because the viscosity acts as a barrier keeping the bubbles apart (Du & Folliard, 2005).

<u>Influence of CEM II/B-V (Cement containing Fly Ash)</u>

Fly ash is one of the major supplementary cementitious materials used in the concreting industry other than CEM I. It has been used to replace a percentage of CEM I in order to save in material usage, thus, reducing carbon emissions that are released during the manufacture of CEM I and the production costs of concrete. Fly ash (or PFA) is a by-product of burning coal during the generation of electricity (Gao, et al., 1997) and as coal fired power stations accounts for 30% of the total electricity supply in the UK (Energy UK, 2015), there is a continuous abundance of fly ash available for concrete. Anthracite (rarely burned in power stations), bituminous, sub-bituminous and lignite are various coal types burned and their chemical compositions are shown in Table 2.5 (Ahmaruzzaman, 2010).

The use of fly ash in concrete is very common in the UK as approximately 5.5 million tonnes is produced each year (UKQAA, 2016). From the amount produced approximately 55% is utilised for the concrete industry as a replacement for CEM I. This aids in the sustainability and reduces the amount of CO_2 produced from CEM I production and manufacturing. The problem with using fly ash in concrete is that the material is unpredictable in how it behaves during durability testing, for example, a scoop of material can have different properties such as fineness and loss of ignition (L.O.I.) compared to a second scoop from the same batch of material.

Table 2.5 Chemical composition of different coal available in the UK and Europe (Ahmaruzzaman, 2010)

Chemical Composition	**Bituminous (wt. %)**	**Sub-bituminous (wt. %)**	**Lignite (wt. %)**
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO_3	0-4	0-2	0-10
Na_2O	0-4	0-2	0-6
K_2O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

Though fly ash has become a major part in the concreting industry, it has become problematic material regarding chemically air entraining this type of concrete. As fly ash is a by-product of the burning of coal, there is still can be high levels of unburnt carbon in the material. If this is the case then the fly ash is unsuitable for use in concrete (Gao, et al., 1997). More importantly, if concrete containing fly ash is to be air entrained then more problems will arise. A major problem that has been and is still being investigated is the prevention of the carbon molecules from absorbing the air entrainer causing the subsequent air content to be reduced (Pedersen, et al., 2010).

Although the majority of carbon is removed (using electrostatic extraction), there is still a minor amount in the fly ash which has been found to absorb the air entrainer, consequently causing a higher percentage of AEA to be used (Helmuth, 1987; Lane, 1991; Bouzoubaa, et al., 2000). Moreover, with the increase in the percentage of AEA the workability is affected causing the concrete to be more flowable, and this will have a significant impact on the hardened properties (Helmuth, 1987).

Concurring with the studies done by Helmuth (1987), Zhang (1996) and Hill, et al. (1997) all determined that with the use of fly ash in concrete, the requirement for AEA increases from two to six times that required for CEM I. Zhang (1996) carried out a series of mixes where the type of air entrainer was varied and the cementitious materials used were CEM I and CEM I/fly ash. The author concluded that CEM I required a much lower dosage than fly ash (Table 2.6) and the various dosage indices are varied depending on the AEA used. The dosage index was derived as a ratio of the AEA required for PFA compared to when OPC is used (calculation shown in Equation 2.2 (Zhang, 1996)).

Table 2.6 Dosage requirement of mixes (Zhang, 1996)

AEA code	CEM I dosage (ml/50kg cement)	CEM II/B-V dosage (ml/50kg cement)	DI
A1	40	144	3.60
A2	70	133	1.90
A3	75	245	3.27
A4	65	288	4.43
A5	40	101	2.53
A6	65	288	4.43
A7	50	288	5.76
A8	80	504	6.30

$$Dosage\ Index\ \ (DI) = \frac{AEA\ required\ with\ PFA}{AEA\ required\ with\ OPC} \qquad 0.2$$

Further to the research conducted by Zhang (1996), Freeman, et al. (1997) investigated the effects of AEA on fly ash concrete and the interactions that occur between them. Determining how fly ash and the air entrainer interacted with one another, a foam index test is carried out. The test consists of a fly ash concrete being titrated with AEA until stable air voids are observed on the surface. The volume of AEA required for the concrete is described as the foam index, and majority of the time with fly ash this value is reported as being high, insinuating that that a large volume of AEA is required to achieve the right air content (Helmuth, 1987; Zhang, 1996; Hill, et al., 1997; Freeman, et al., 1997; Hachman, et al., 1998; Pedersen, et al., 2008).

Not only is the amount of unburnt carbon a factor of the air entrainment but also the particle size. Kulaots, et al. (2004) studied the effects of different particle sizes of unburnt carbon on the air entrainment looking at which particle sizes adsorb more of the AEA. Fly ash classes C and F, inorganics content (SiO_2 + Al_2O_3 + Fe_2O_3) of above 50% and 70% respectively, were used with varying particle sizes. They found that the finer particles adsorbed more of the AEA than the larger particles due to a higher surface area of the finer particles and greater accessibility (BSi, 2012).

Influence of CEM III/A (Cement containing GGBS)

Ground granulated blastfurnance slag (otherwise known as GGBS) is the resultant waste material from the production of pig iron. It is estimated 300 kg of GGBS is produced for every tonne of pig iron manufactured (Neville, 2011). Slag cements have a similar composition to that of CEM I with majority of the oxides being contributed by lime (or calcium oxide). Table 2.7 shows the comparison between the two materials.

Table 2.7 Comparison of oxide content in Portland and slag cements (Neville, 2011)

Oxide	CEM I	CEM III/A
Lime (%)	60 – 66	40 - 50
Silica (%)	18 - 25	30 – 40
Alumina (%)	3 -10	8 – 18
Magnesia (%)	0.5 - 4	0 - 8

Using GGBS in concrete construction is not an uncommon practice as it is another approach to reducing the subsequent CO_2 that is released when CEM I is manufactured. Though this is observed to be an advantageous way to reduce carbon dioxide emissions, there are problems arising with the entrainment of air in slag cements. Deja (2003) noticed that there were a number large discrepancies in studies carried out in regards salt scaling resistance which postulated that although a low water/cement ratio was used (less than 0.45) with a high air content, CEM III/A is not sufficient enough to perform in freeze-thaw conditions. The consensus of the research community is that GGBS has a lower number of air voids which coincides with the fineness of GGBS which is finer than CEM I but again a number of authors (Luther, 1994; Stark & Ludwig, 1997) have observed a lower effectiveness of air entrainments in the mix due to a denser microstructure of the paste which prevents water reaching the expansion voids.

Although there is contradiction as to whether air entrainment aids in the protection against freeze-thaw there are studies which suggest that the particle size increases the strength of CEM III/A concrete, thus, freeze-thaw durability. Wang, et al. (2005) looked at the effects of various sizes of GGBS particles (up to 125µm) on the compressive strength. The authors found that with the decrease in the particle size there was an increase in the compressive strength concluding that the finer particles largely contribute to the strength development.

If and when the entrainment of air in CEM III/A has been achieved, there is no guarantee that said protection would actually increase the durability of the concrete (Deja, 2003). However, a theory has been suggested that increasing the curing time of the concrete will in fact improve the air entrainment (Stark & Ludwig, 1997). Giergiczny, et al. (2009) explains that the use of air entraining admixtures in CEM III/A concrete had to have nearly double the requirement that standard CEM I uses, in addition, when increasing the GGBS content the volume of air in the hardened concrete decreased as a result. Even though the GGBS is known to reduce the concretes durability during freeze-thaw attack in terms of the Swedish freeze-thaw test method (SS 137244), it classifies CEM III/A concretes as ‘good’ as the mass lost was less than 1.0 kg/m^2 at the end of the 56 cycles.

Influence of CEM II/A-L (Cement containing Limestone)

CEM II/A-L is concrete with limestone addition which has recently been introduced to replace a certain percentage of CEM I. Similarly, to fly ash and GGBS it is used to replace a percentage of CEM I to help reduce the amount of CO_2 released into the atmosphere. What makes limestone different from fly ash and GGBS is that it is given the term filler which signifies that the cementitious material is naturally occurring and not a by-product from the manufacturing industry. Limestone is ideal for replacement in concrete due to the material being chemically inert though they have been known to have minor (if any) hydraulic properties (Neville, 2011).

Using chemical admixtures with limestone is not uncommon and with British Standards allowing the use of up to 20% addition in the concrete mixes the use of admixtures is a requirement. Work done by Detwiler (1996) describes several mixes were cast of both CEM I and CEM II/A-L with the addition of fly ash, water reducing and air entraining agent. The test used CEM I and limestone cement from the same clinker from the same plant. Both CEM I and limestone cement were sieved through a 44μm sieve retaining 3.9% and 4.2% respectively. Once cast, the cylinders were cured for 7 days in water then taken out to air cure until the test age. Using CEM II/A-L concrete, an increase in the air entrainer was required to meet the target air content. As a result, the compressive strength data shown in Table 2.8, depicts near perfect compressive strengths with the unit weight of the CEM II/A-L samples being slightly higher.

Table 2.8 Compressive strengths of test concretes (Detwiler, 1996; Detwiler & Tennis, 1996)

Cement[1)]	**Fly Ash Content and Type**	**Cement Content, kg/m^3**	**Unit Weight, kg/m^3**	**7 days, MPa**	**28 days, MPa**	**56 days, MPa**
CEM I	0	362	2270	29.4	36.1	39.5
CEM II/A-L			2305	29.4	36.7	41.1
CEM I	15%	362	2250	22.7	30.1	30.5
CEM II/A-L	Class F		2300	24.6	31.7	36.5
CEM I	15%	308	2295	18.8	25.0	27.2
CEM II/A-L	Class F		2245	19.1	23.9	28.2
CEM I	25%	308	2290	23.6	30.9	30.4
CEM II/A-L	Class C		2310	23.1	30.3	29.0

[1)]Where CEM II/A-L has 2.5% limestone addition.

Ordinarily, results shown in Table 2.8 would be put in question as it is unusual for a binary concrete to have a higher strength than CEM I. This is in relation of the particle size of the limestone. Knop, et al. (2014) considered the packing of particles in the concrete (similar to the density model of grain mixtures

Stovall, et al. (1986)) to increase the surface area of the particles, thus, the density and reduce the porosity but also to ensure that no spaces between the larger particles was unoccupied.

The study looked at the effects of various particle sizes on compressive strength and rate of hydration. Mortar mixes included a single particle size distribution and a combined particle size distribution (53μm, 25μm and 3μm) which were larger and smaller than a CEM I particle (mean particle size of 17μm) with different addition percentages. The mortars containing a single particle size was found to be the following:

- Particles larger than CEM I reduced the surface area of the mortar and slowed down the rate of hydration which increased with the rise in the addition content;
- Particles of similar sizing to CEM I showed coinciding results for the rate of hydration whether addition of limestone was added or not; and
- Particles smaller than CEM I increased the surface area and rate of hydration.

Combined particle sizes were also tested varying mortars of different particle size combinations but fixing the addition content at 5%, showing an increase in the rate of hydration compared to CEM I

2.5.4.2 Effect of Compaction by Vibration

Vibrating the concrete once it has been cast is an important part of concreting and is a necessity for concrete structures in order to ensure full compaction is achieved (Juradin & Krstulovic, 2012; Bratu & Pintoi, 2014; Tian & Bian, 2014). According to Ramachandran (1984) as the vibration process is carried out, the air content of the concrete decreases as the vibration time increases. This will rapidly decrease the air content (as required) because the larger air bubbles are easily removed. However, as the bubbles are removed, the thickness of the concrete that overlays the trapped air becomes thicker making it more difficult for the bubbles to escape (Ramachandran, 1984). Furthermore, if the vibration time extends any further than three minutes, the consequence is a loss of the entrained air can be as much as 50% with there being a possibility of segregation occurring (Dodson, 1990).

2.5.4.3 Effect of Temperature

Temperature effects the volume of entrained air there is in the concrete. The effect of temperature on the air entrainment is a phenomenon not regularly seen. In concrete, air entrainment is seen to work better at higher temperatures rather than colder that causes an increase in the volume of air. However, during the hydration process, water is taken up by the cement meaning that there is a dramatic decrease in the availability of water for the foaming process. Thus, at higher temperatures there is a reduction in the volume of entrained air (Cornelius, 1970).

2.5.4.4 Effect of Admixtures, Dosage and Type

Using various admixtures will require different dosages to be used depending on the type of AEA in order to meet a specified air content. The more air entrainer used in concrete, the higher the air content.

The combinations of different admixtures used in the concrete along with AEA have been considered (Lazniewska-Piekarczyk, 2013a) whereby various viscosity modifying admixtures (VMA) and superplasticizers are used coinciding with the use of AEA. Lazniewska-Piekarczyk (2013a) varied admixture types and looked at how VMA influence the air entrainment and workability when used with AEA. Figure 2.14 illustrates the interaction between aggregate-cement-water along with air entrainer in self compacting concrete.

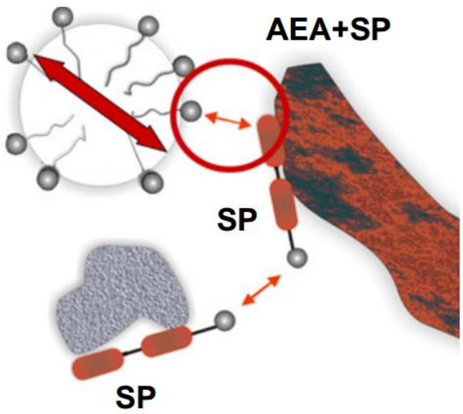


Figure 2.14 Arrangement of aggregate-cement-water particles with AEA (Lazniewska-Piekarczyk, 2013a)

The author concluded at the end of the study that with a wide range in different VMA and AEA available on the market it can be difficult to find compatible admixtures to work together. The author found that, VMA has both beneficial and hindering effects on the air entrainment. This is due to the type of VMA and AEA. Each admixture produced tends to have different chemical properties so no two are the same. Even though there is a reduction on the strength and although the freeze-thaw resistance does meet that of the European Standard, there is still significant resistance to freeze-thaw attack.

Further to this research Lazniewska-Piekarczyk produced another paper (2013b) describing and explaining the interactions between superplasticizer (SP), anti-foaming admixtures (AFA), AEA and VMA in self compacting concrete and also looks at the variation of air content when admixtures that have a side effect of entraining air. The author found that with a wide range of different admixtures used, there were different effects regarding the air content and workability. Such results included that varying the VMA only, one concrete had its air content decreased whilst in another increased the air content so the author concluded that with a difference in the chemical components in the admixtures, there was a range in the results which was a product of said component differences.

2.5.4.5 Effect of Mixing Time

Ramachandran (1984), Chitla, et al. (1991) and Neville (1995) all have stipulated similar points about the mixing. When a concrete's constituents are placed into the mixer with air entrainer, the mixer agitates the AEA causing it to foam and stabilize the voids. It has been determined that increasing the speed of the mixer causes more air to be entrained.

Increasing the length of time along with the speed will slightly increase the air content in the concrete, but with prolonged mixing, the air content will begin to decrease as a result. Reductions in the air content can arise because of worn components on the mixer or by simply overloading the mixer (Ramachandran, 1984).

2.5.4.6 Effect of Fine Aggregates on Air Entrainment

Fine aggregates are an important part of a concrete mix design as they improve the strength and durability of the concrete. One area which is seen to be of 'paramount importance' (Scripture & Litwinowicz, 1949) regarding air entrainment. Air content in concrete is significantly affected by the fine aggregates, primarily, the quality and grading of the sand used (Scripture Jr, et al., 1948). A study done by Kennedy (1943) found that the size grading below a certain mesh size (No. 14 sieve which is 1.41 mm) starts to influence the air entrainment. Though the work carried out was only done on mixes which consisted of sand, water and air entrainer meaning that the results produced are called into question, hence, not a lot of conclusions could be made.

Though the conclusions made were that a decrease in the air entrained was caused by a reduction in the fineness of the sand. That is to say, once the grading reaches No. 28-48 sieve (0.595-0.297 mm respectively) the requirement for entrainment decreases dramatically (Scripture Jr, et al., 1948). However, Craven (1948) stipulated that with the fineness of the sand decreasing, the percentage requirement of air entrainer increases.

In terms of sand grading regarding the effect on air entrainment, there has been a wide discussion as to how it affects the said air entrainment. As reported by Kennedy (1943), the grading has a considerable effect in a sand-water mix, yet the grading is stated to have little effect on mortars and concretes (Scripture Jr, et al., 1948). Contrary to Scripture Jr, et al. (1948), Walker & Bloom (1946) believe that there is a relationship between volume of entrained air in the concrete and the fineness modulus (empirical value which determine how coarse or fine an aggregate is).

The articles above describe studies that were conducted on mortar and concrete containing various fines and the effect on the air entrainment. Since then a number of studies (Du & Folliard, 2005; Neville & Brooks, 2010) have identified that fine aggregates do not affect air entrainment until the particle sizes pass the No. 30 sieve (0.595mm). Particle sizes between ranging between No. 30 and No. 100 sieves (0.595-0.149mm) are found to prolong and promote small bubbles within the concrete system. However, fine material passing the No. 100 sieve (0.149mm) is seen to hinder the formation of small bubbles due to shearing of the fine material whose sizes are closely packed to the bubbles.

2.5.4.7 Effect of Coarse Aggregates

Pigeon & Pleau (1995) stated that coarse aggregates do not influence the entrainment. This is because concretes that have larger aggregates tend to have a reduced paste content, thus, a reduction in the requirement for air entrainment. This statement concurs with previous work done by Klieger (1952, 1955) where he found that the aggregate grading has a distinct effect. The problem with these studies were that they do not consider the implications of the type of aggregate used. Various types of coarse aggregates are available for concrete batching but with different properties such as natural gravel compared to granite.

Romano, et al. (2015) conducted studies which looked at the effects of air entrainment and aggregate grading on the fresh and hardened properties of mortars and found that the porosity of the mortars in the fresh state was attributed to the air entrainment whilst the aggregates affected the porosity in the hardened state. Though it can be stated that the grading of the aggregate does not affect the air entrainment, hence, do not interconnect between each other, they both however affect the total air content on the concrete, therefore, influence freeze-thaw durability.

Dodson (1990) added that there are other points that maybe need to be considered. He says that when coarse aggregate is used, especially crushed, there tends to be a high amount of dust on the surface meaning that this can affect the air content by reducing the volume of air. Also, that using stone rather than gravel as the coarse aggregate will cause a reduction in the air that is entrained (Dodson, 1990).

2.6 Influence of Air Void Parameters on Concrete Damage

The current understanding is the air void structure of a sample can reduce and even prevent the damage of freeze-thaw. Sun & Scherer (2010a) discuss the various mechanisms that affect the concrete internally and externally and detail how air voids play a part in the reduction of the damage. The paper looks at the offset thermodynamic properties between the concrete surface and the ice layer which is effectively looking at how the glue-spalling theory is applied. The results show that when the samples are not air entrained, immediate damage due to high hydraulic pressure to the concrete specimen (Sun & Scherer, 2010a) however, with air entrainment damage does occur at the same temperature as non-air entrained but the damage has been reduced.

It has been suggested by the authors that although proper air entrainment is accomplished there is still pressure being applied in the pores causing damage. Sun & Scherer (2010a) have said that they have possibly identified the cause of this damage. It is suggested that in the mesopores (pores which are between 2 µm and 50 µm) there is a considerable ice build-up which forces the water in the pores to move to the voids which then causes crystallization pressure. With the pressure applied to the void walls due to crystallization and the contraction of the specimen due to the freezing temperatures, there is the possibility of damage to the concrete due to fatigue if there is a continuous freeze-thaw cycle (Sun & Scherer, 2010a; 2010b).

2.6.1 Influence of Pore Size Distribution

Pore size distribution is an important influence on concrete properties and other materials regarding the pore structure parameters (porosity and pore size distribution), though it is difficult to correlate the strength results with the porosity to determine how one influences the other. A number of researchers (Luping, 1986; Atzeni, et al., 1987; Iza, et al., 2000) have tried to correlate between strength and porosity (Table 2.9) by expanding on previous work and adopting further variables to create a model that provides said correlation.

Table 2.9 Previous model equations adopted to correlate between strength and porosity

Mathematical Law	Author	Equation	Correlation, %
Linear	Hasselman (1964)	$\sigma = \sigma_0 - Kp$	53
Power	Balshin (1949)	$\sigma = \sigma_0(1-p)^m$	54
Exponential	Ryshkevitch (1953)	$\sigma = \sigma_0 e^{-Kp}$	51
Logarithmic	Schiller (1958)	$\sigma = Kln\left(p_{0_s}/p\right)$	55

Where:

σ = compressive strength at porosity p
σ_0 = compressive strength when porosity is zero (p_{0s})
K & m = empirical constants

Using the previous models, Kumar & Bhattacharjee (2003) conducted a study to find a model that would better correlate the strength and porosity. They tested a series of concrete cores measuring 75mm in diameter and 100mm in length that were taken from CEM I beams with w/c ratios of 0.38-0.65. The models found to have inadequate correlations with the best model providing a correlation between the strength and porosity to be 55%. They concluded that with the inclusion of multiplying factors to the model for various parameters like the cement type and content, aggregates, age, temperature and exposure to acidic environment; a better correlation was found to be upwards of 85%.

Lian, et al. (2011) developed the model further by including Griffith's model of fracture (Griffith, 1920) of pores inside the concrete. The theory relates mechanical performance with porosity that includes Young's modulus and the fracture energy to determine the compressive strength when the strength of the hardened cement paste is not available. In doing so they managed to develop a model that would provide a correlation up to 99%.

Trying to classify the various sizes that are observed in the microstructure is a difficult task. During the studies above, it was identified that there are four types of pores which reside in the concrete matrix (Gregg & Sing, 1982; Kumar & Bhattacharjee, 2003; Brandt, 2009; Sun & Scherer, 2010b):

- Gel pores which are a specific type of micropores typically sized between 0.0005µm and 0.01µm;

- Capillary pores are related to the mesopore group measuring between 0.01µm and 10µm but average diameter between 0.02 and 0.03µm;
- Intentionally entrained air voids as a result from air entrainment range between 0.05µm and 1.25mm;
- Air void larger than capillary pores which have been entrapped during the mixing process.

Figure 2.15 shows a graphical scale of the pore size distribution and how they range against one another (CEB, 1992; Kumar & Bhattacharjee, 2003).

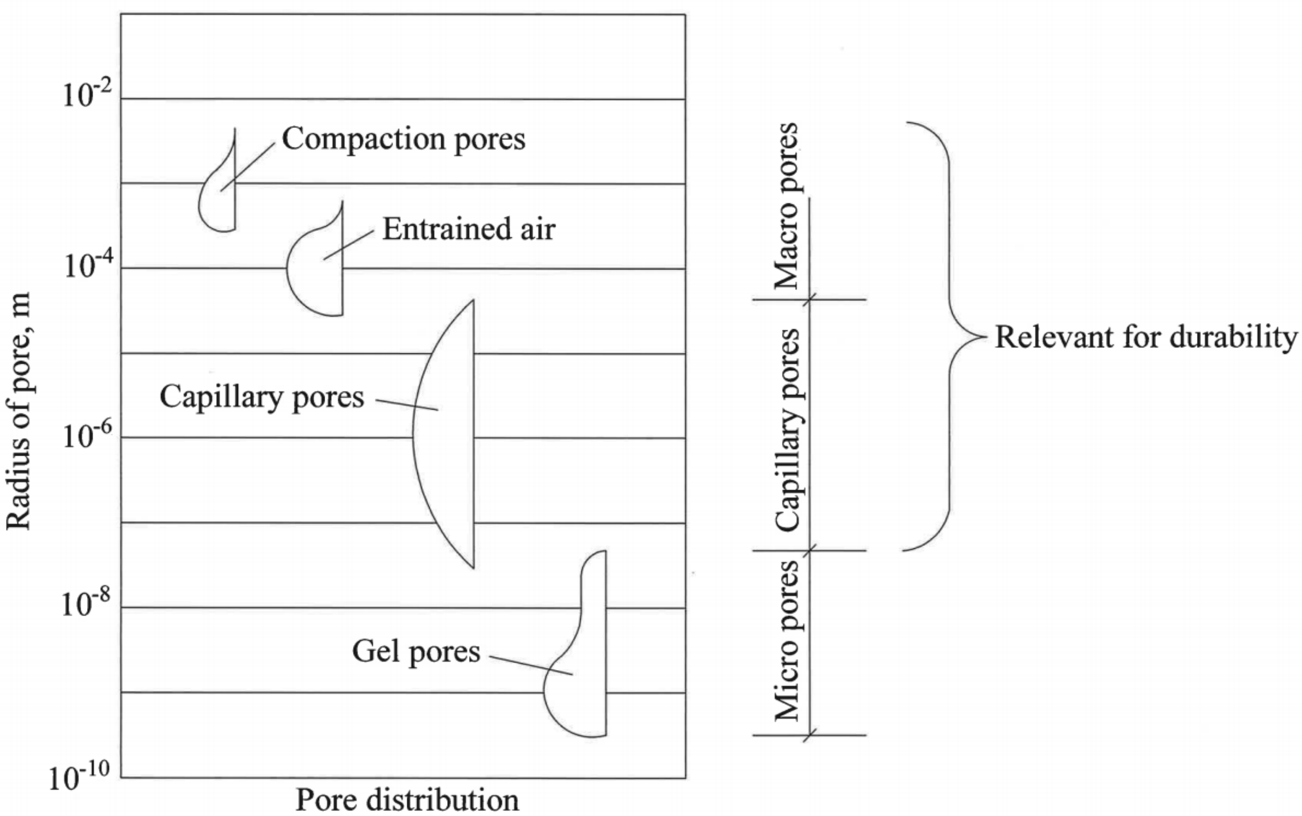


Figure 2.15 Graphical scale of pore size distribution (CEB, 1992)

Das & Kondraivendhan (2012) details work done for determining the pore size distribution through three different tests (compressive strength, permeability and hydraulic diffusivity) on three different strengths (20-40 MPa) of CEM I concrete. Figure 2.16 and Figure 2.17 show the porosity and mean distribution radius respectively plotted against concrete age for three concretes that were used to determine the effects of pore size distribution. Figure 2.16 shows with the decrease in the water/cement ratio, the porosity decreases along with it though from Figure 2.17, with the reduction in the water/cement ratio there is a decrease in the mean distribution radius meaning a better pore refinement (Das & Kondraivendhan, 2012; Chen & Wu, 2013). This coincides with the results produced by Lian, et al. (2011) where the compressive strength decreases as the total porosity increases.

Further work done by Zhang & Taylor (2015) looked at how the pore size distribution influences freeze-thaw durability. Mixes consisting of silica fume (5% addition) and fly ash (Class C 20% addition) with varying water/cement ratios were tested. The samples were analysed using MIP to determine the pore size distribution before freeze-thaw testing. Samples oven dried until a constant mass was achieved to remove remaining water and its effects that the excess water may have.

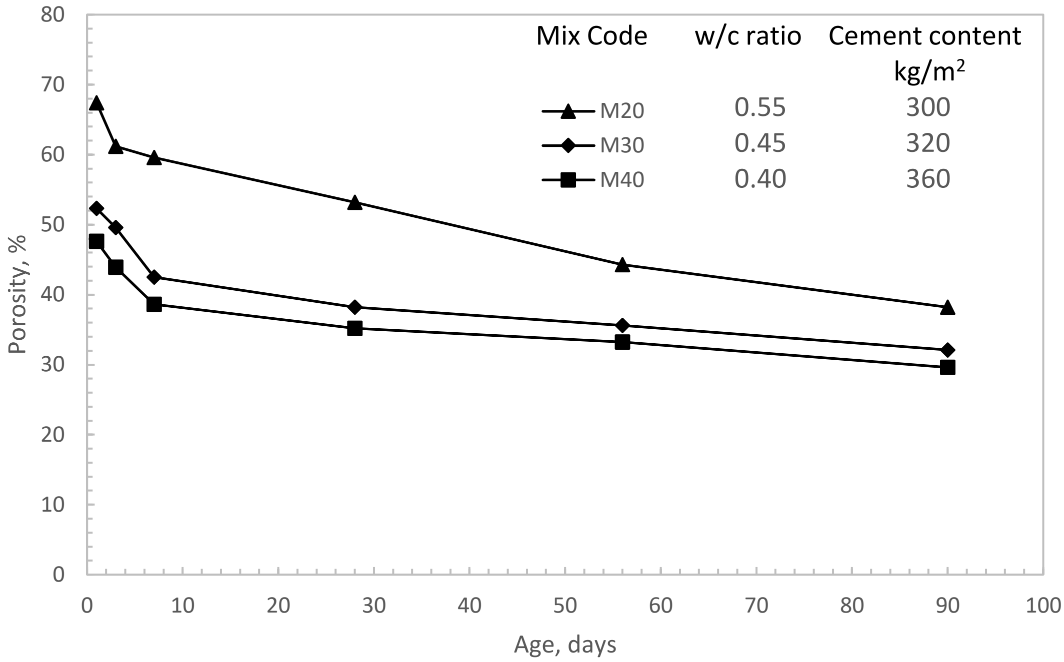


Figure 2.16 Porosity against concrete age for CEM I concretes of different w/c ratios (Das & Kondraivendhan, 2012)

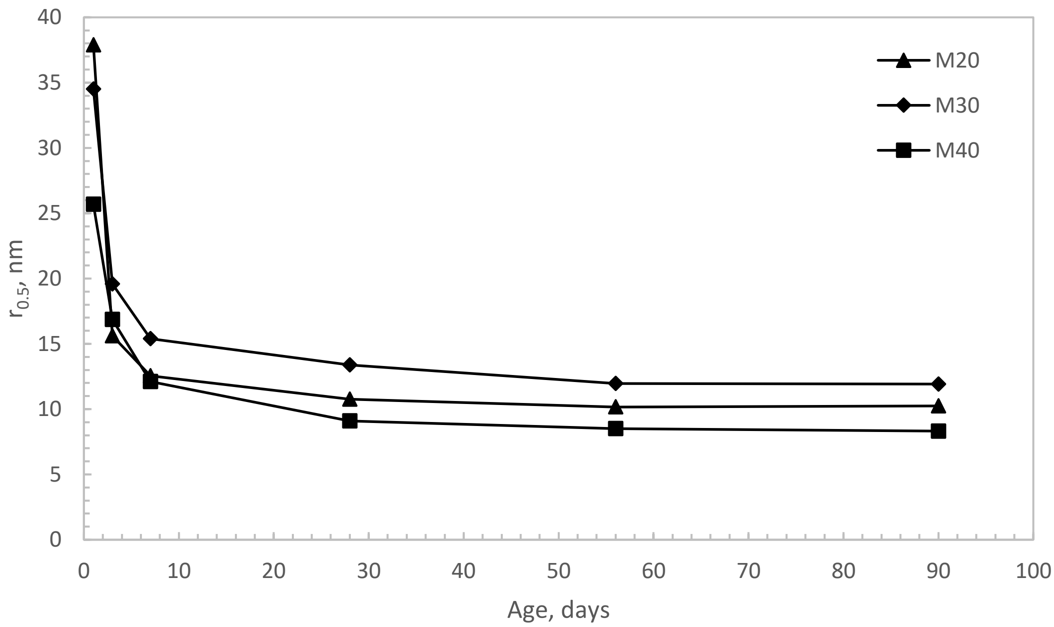


Figure 2.17 Mean distribution radius ($r_{0.5}$) against concrete age for CEM I concretes of different w/c ratios (Das & Kondraivendhan, 2012)

The authors concluded that increasing the water/cement ratio increased the porosity of the sample as described by Das & Kondraivendhan (2012). The resulting freeze-thaw tests showed that the finer pores (smaller than 0.04µm) and the coarser pores (larger than 0.2µm) provided good protection with regards to freeze-thaw. However, intermediate pores (0.04 – 0.2µm) were found to provide the least protection. A study by Kondraivendhan & Bhattacharjee (2010) found that in regards to the strength of a concrete sample, there is a relationship with the pore size whereby finer pores infulence the strength less than larger which is observed from Figure 2.16 and Figure 2.17.

2.6.2 Spacing Factor

As mentioned earlier, the spacing between the bubbles is determined by the Powers spacing factor which calculated out to be 250 µm (Powers, 1945), though nowadays that value has been changed to 200 µm. This is calculated by determining the volume of small pores (only as entrained air bubbles are assumed to have small diameters) as a proportion of the total volume of pores (Walker, 1980).

Powers spacing factor assumes that the bubble sizes are all the same size. Of course, this is not the case which means that in using this theorem, consideration must be done in terms of the bubble sizing. The spacing factor was formulated through the theory that hydraulic pressure was the main cause of the frost damage. Though nowadays, it is not the main cause but rather one of many causes which have to be considered in order to determine an overall mechanism for frost damage (Hasholt, 2014).

Hasholt (2014) looked at four different studies to test the spacing factor theory: (1) the effect of compaction, (2) the different combination of admixtures in the concrete, (3) the effect of mixing, and (4) the effect of pressure during hardening. It was concluded that each study provided a varying outcome when tested, but one major discovery which was made was that the spacing factor does not affect the total mass loss during scaling.

The value of 250 µm has been mentioned a number of times (Powers, 1945; Powers & Helmuth, 1953) as the reference spacing factor for concrete as many studies and field work has shown this value to be acceptable. However, it was established that a value of between 100 – 200 µm depending on the cement type to be more suitable (Backstrom, et al., 1958). That being the case then there is controversy between which values to use. Though the value of 200 µm has been adopted by many governing bodies as the official limit for the spacing factor, Pigeon, et al. (1986) explains that there exists a *critical spacing factor* when a concrete is subjected to freeze-thaw, there is a limit before the concrete deteriorates rapidly.

2.6.3 Identifying and Mitigating Air Void Loss

Loss of bubbles during the concrete's fresh state is a major concern when air entrainment is a necessity for durability. The loss is a problem because concrete is generally designed to behave in a specified way or to have a percentage of air content, however, the bubbles in the mixture have been seen to escape rather than entrained. Ley, et al. (2009) produced a paper suggesting that there are three observations where bubbles have seen to escape from both air and non-air entrained concrete:

2.6.3.1 Paste expansion

A plastic bottle was filled to the top and sealed and laid on its side. Once the bottle was sealed, the hydration process began which caused the bottle to swell as a result of an exothermic reaction. Further observations shown that when the swelling began, the voids were agitated and rose to the top where the bleed water was located (Ley, et al., 2009). It was observed that as the paste expanded it pushed the bubbles against the side of the bottle forcing the textured surface (or shell), which has formed to on top, to crack allowing the neighbouring bubbles to interact with each other.

2.6.3.2 No paste expansion

Similarly, with the method above, a bottle was filled with concrete but this time only 75% was filled and the remaining 25% with pretend bleed water to prevent mixing to occur. It was observed that concrete with air entrainment had little variation of the bubble's sizes and the diameters of bubbles did not change over an eight-hour period. The non-air entrained concrete however, observed smaller bubbles gradually shrink whilst larger bubbles continued to increase in size. Bubbles that lay between these sizes remained constant. This is explained by Fagerlund (1990) whereby smaller voids have a high-pressure state whereas the larger bubbles are in a state of low pressure, so the bubble distribution tries to reach a state of equilibrium.

2.6.3.3 Loss caused by fluid pressure

As with method two, a bottle is filled 75% of the way with concrete but the remaining 25% if filled with fluid, however, the fluid which the bubbles are located had its pressure increased to 0.7 bar above the atmospheric pressure with two different fluids (vinsol resin and tall oil) were used in the test. The resultant pressure variant showed that the bubble shells vary between each of the fluids used. Furthermore, the colour of the shells and the particle size were different though there was no known conclusion due to this unusual process. Moreover, increasing the atmospheric pressure displayed a decrease in bubble volume by 58%.

2.7 The Use of Admixtures in Concrete

2.7.1 Air Entraining Admixtures

In the concreting industry, there is a vast variety of concrete air entraining admixtures available to choose from. Table 2.10 provides a series of various chemical admixtures used during concrete casting. Though there is a wide selection, Dodson (1990) described that today's air entrainers can be placed into three categories: anionic, cationic and non-ionic. Anionic types of acids are the most common used in concrete entrainment because of their very good stability of the air void. Common acids in this group are abietic acids that include wood resins. Other acid such as fatty acids belong in this group (Rixom & Mailvaganam, 1986).

Table 2.10 Admixtures available and their purpose and benefit

Admixture type	Purpose	Effect	Practical example
Accelerators (Aitcin, 2016b)	Speed up the chemical reaction between water and cement.	-Reduced setting times. -High early strength. -Normal strength/time at low temperatures	-Offsetting low temperatures in cold weather. -Early removal of formwork.
Air entraining agents (Gagne, 2016a)	Stabilize air bubbles during hardening process.	-Improved workability. -Improved consistence.	-Good protection against freeze-thaw attack.
Anti-freezing agents (Aitcin, 2016c)	Reduces the freezing temperature of the water in the concrete.	-Prevents concrete from freezing under low temperatures. -Extra protection for steel reinforcement.	-Concreting in cold climates where temperatures are very low such as Finland, Russia and Poland.
Anti-washout agents (Euclid Chemical, 2017)	Prevents loss of fine material during underwater concrete placement	-Reduction of the bleed water from the concrete. -Eliminates expensive de-watering during underwater construction.	-Underwater casting and repair.
Corrosion inhibiters (Aitcin, 2016d)	Delay the ingress of chloride ions into the concrete.	-Protective layer around steel reinforcement -Raises the corrosion threshold	-Used with elements containing high steel reinforcement.
Expansive agents (Gagne, 2016b)	Increase the concrete volume during hydration	-Increase to the volume of concrete. -Decrease cracking from drying shrinkage.	-Reduction of cracking of concrete slab from drying shrinkage.
Pumping aids (Prior, 1972)	Increase flow of concrete through pumping.	-Decrease pressure used for pumping. -Reduction of internal friction. -Less chance of segregation occurring.	-Pumping high volumes of concrete to a site. -Long pumping distances.

Table 2.10 (cntd) Admixtures available and their purpose and benefit

Admixture type	Purpose	Effect	Practical example
Retarders (Aitcin, 2016a)	Delay the length of time of hydration reaction.	-Retained workability. -Extended setting times. -Higher ultimate strengths.	-Offsetting the effects of high ambient temperatures. -Preventing cold joints between pours.
Shrinkage reducing agents (Gagne, 2016c)	Decrease shrinkage cracks	Used alone or in conjunction with air entraining and expansion agents to: -Increase durability of freeze-thaw. -Reduce severe cracking.	-Prevents cracking occurring when w/c ratio is below 0.4.
Superplasticizers (Nkinamubanzi, et al., 2016)	Very high separation of cement.	-Very high workability for a given water content. -High water reductions for a given workability.	-Aiding in concrete placing in difficult situations i.e. tightly packed reinforcement. -Early high strength.
Viscosity modifiers (Palacios & Flatt, 2016)	Control the stability and cohesion of concrete with particular rheological properties	-Increase the flow of concrete with higher fines content. -Increase cement hydration -Reduction of water absorption	-Use with self-compacting concrete allowing a flowable concrete through compacted reinforcement.
Water reducers (National Precast Concrete Association, 2013)	Separation of cement and increased rate of hydration.	-High workability for a given water content. -Higher strengths for a reduced water content at a maintained workability.	-Denser and stronger concrete. -Better compaction. -Cheaper concrete.
Water resisting (Dransfield, 2010)	Reduce the water absorption/ transportation of water through the concrete surface.	-Reduction in water absorption. -Increased strength in wet climates.	-Concrete casting during precipitation. -Reducing water affecting fresh concrete properties.

Air entraining agents have been around for many years and have been considered to be one of the more important admixtures used in concreting (Jackson & Dhir, 1988; Pistilli, 1983). Ideally, the bubbles that form in the concrete are uniformly distributed, small and with an approximate size range of 0.25mm to 1mm. Many of these air entrainers were originally based on natural resins, animal or vegetable fats or synthetic detergents during the mixing stage (Jackson & Dhir, 1988; Gagne, 2016a).

Naturally, there are benefits to using air entrainers in the concrete. These benefits include the interruption of the capillary pores which will reduce the permeability of the concrete and, more importantly, to reduce the internal stresses of the concrete during the expansion of ice. Other advantages included the reduction in water and cement, temperature and alkali expansion (chemical reactions that occur between the cement and certain aggregates) (Blanks & Cordon, 1949) and other benefits which were not identified as being possible advantages for air entrainers; the workability of the fresh concrete has increased with the addition of the AEA and there has been a reduction in the segregation and bleeding as a result (Jackson & Dhir, 1988; Gagne, 2016a; Nkinamubanzi, et al., 2016).

Though, using AEA has consequences in terms of the concrete's durability. Whilst the performance during freeze-thaw attack is significantly increased, the strength of the concrete is reduced as a result of the bubble formation. Adjustments can be made to the water content to keep the strength reduction to a minimum (Dodson, 1990).

2.7.2 Chemical Structure of Air Entraining Admixtures

For a complete understanding of the mechanics of how air entrainers work in concrete, a discussion of the chemical and physical properties were outlined so that a basic understanding of the formation and maintenance of said bubbles can be produced.

According to Chitla, et al. (1991) most air entraining admixtures are what are known as hydrophobic, surface active compounds. This means that the compounds are repelled from a mass of water, though there is no repelling force (like two matching sides of a magnet) it just means that there is not attraction between the compound and water. In regards to air entrainers, these surface active compounds consist of a non-polar (hydrophobic) hydrocarbon attached to a polar (hydrophilic) group that consists of -COO^-, -SO_4^- or -NH_3^+ as depicted in Figure 2.18 (Chitla, et al., 1991). When this happens, the surface tension of water is lowered which contributes to the generation of bubbles and prevents the bubbles from coalescing (Chitla, et al. 1991, Marchon, et al. 2016).

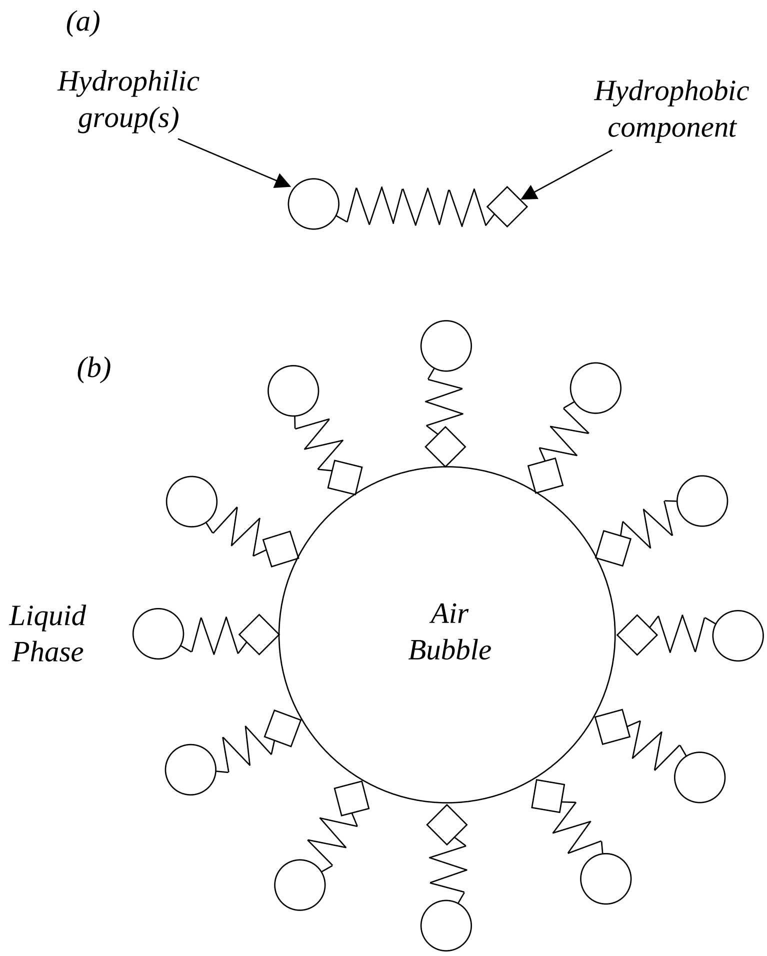


Figure 2.18 Illustrated representation of surface active molecules (a) surface active and; (b) stabilized air bubble (Chitla, et al. 1991, Du & Folliard 2005)

2.7.3 Formation and Stabilization of Air Entrained Bubbles

A common misconception about what an air entrainer' s role is regarding the formation and stabilization of bubbles. Air entraining admixtures do not form or generate bubbles in the concrete but purely stabilize the already formed or existing bubbles in the concrete mix (Powers, 1968; Ramachandran, 1984; Dodson, 1990). In terms of stabilizing the bubbles in the concrete, Dodson (1990) outlines the following methods; (1) enclose the bubbles during the mixing process, (2) mixing the AEA with the water, (3) initially present in the voids in the cement and aggregate, or (4) inside the pores of the aggregate.

Dodson (1990) explains that even though air is being purposely entrained which is an addition to the total mass of the concrete, the air being entrained is done so in the cement paste only. There has been time where air has congregated at the cement/aggregate interface, but this is an uncommon occurrence and is only seen when vast quantities of admixture is used.

Mielenz, et al. (1958) explained in an earlier paper that air in fresh concrete is obtained by four different origins, detailing that these are the only sources of bubbles in concrete whether air entrainers are used or not. These origins are: (1) air already present in the spaces between the cement and aggregate; (2) air in the cement and aggregate particles but are forced out during the hardening process and the ingress of water; (3) air which is already mixed with the water; and (4) air which is folded into the concrete during the mixing process.

Mielenz, et al. (1958) makes a clear point in their text stating that these sources listed above are the only origins which bubbles are entrained in the concrete. The authors are correct in terms of how bubbles are ‘entrapped’ in the concrete, but it is a requirement to make them ‘entrained’ which is the more difficult part, and this involves the use of AEA.

The main method is bubble formation through emulsification. As described above, bubble formation is the result of the mixing process and this mixing process forms an emulsion which is a term used for a composition that is typically labelled as unmixable, for example oil and water. To produce the emulsion, two methods have been identified as ways to form bubbles in the mix; first being the immersion of air due to the vortex action created when the concrete is mixed, the same vortex action when water runs down a plug hole. The other method being a ‘three-dimensional screen’ which is formed when the fine aggregates descend on top of itself (Du & Folliard, 2005; Powers, 1968).

2.7.4 Air Void Collapse

Air voids, whether they be in a foam or concrete system, are thermodynamically unstable as in they involve thermodynamic conditions which the purpose is to reduce the total boundary area between phases (Myers, 1999). Air void coalescence is the result of when two or more bubbles merge together to form a larger bubble. In terms of bubbles in foam, whereby multiple bubbles are interconnected, there is a possibility that the bubbles in the foam will collapse due to capillary flow (Myers, 1999).

When multiple voids are connected, a liquid region is created forming foam and within the liquid region of the foam. When the bubbles in the foam reach a roughly stable state, a large curvature will exist that is greater than the thin films which form the bubbles themselves (Myers, 1999). These films, once connected to one another, for a network of connecting bubbles which are connected by plateau borders and when connected act, as Myers (1999) describes, as capillary pumps whereby air is pumped from one bubble to another. This is due to the pressures which have built up internally in the bubbles in comparison to the external pressure which should be less. For the bubbles to remain stable, the pressures inside the bubbles must remain equal. If there is a shift in the pressure it will lead to capillary pumping and cause the subsequent smaller bubbles to collapse and merge (Myers, 1999).

2.8 The Microstructural Air Void Parameters of Concrete

2.8.1 Methods for Determining the Microstructural Air Void Parameters

Determining the microstructural air void parameters of hardened concrete is understood to influence how concrete behaves during freeze-thaw. It has been established that since its derivation, the Powers spacing factor theory has provided a benchmark for ensuring that concrete endures freeze-thaw. However, recently further studies (Elsen, 2001; Hasholt, 2014) have suggested that other parameters play a part in a concrete's durability. These parameters are determined in one of two ways; linear traverse method or modified point count method.

2.8.1.1 Linear Traverse Method

This is the conventional method to analyse and calculate the microstructural air void parameters detailed in both BS EN 480-11 and ASTM C457. The method entails a microscope to traverse (move) along a line identifying either a void, aggregate or paste (Figure 2.19a) and an operator to tabulate the chord (void) lengths at different phases and recording the data for analysis. Using this analysis, it allows for simple calculations to be carried out to determine the air void parameters by summing up the total lengths of voids and the total number of occurrences of each of the phases (FHART, 2006). Using this method however does have its problems. The calculations are sensitive to any errors that may occur during the test and this sensitivity will affect other results.

2.8.1.2 Modified Point Count

Used only in ASTM C457, this method uses a grid system (Figure 2.19b) whereby a microscope passes over regular points and the composition of the sample is determined identifying each phase as observed. Similarly, to the linear traverse method, the air void parameters are calculated using simple, yet sensitive equations. Moreover, using this method such as establishing the paste-aggregate boundary so a further pass over with the microscope is required to determine the properties.

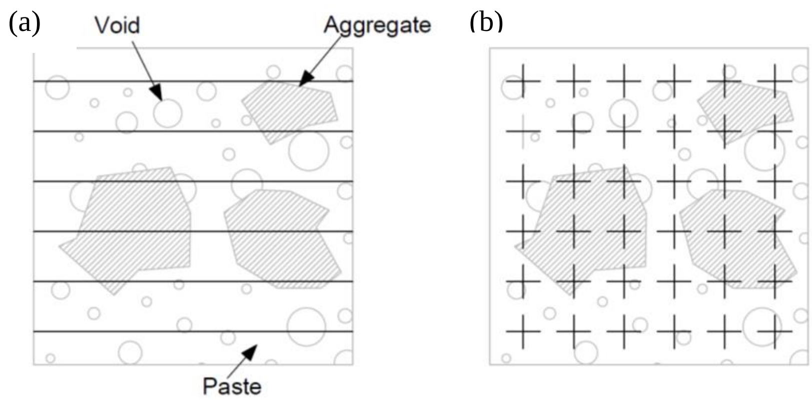


Figure 2.19 Different methods to quantify air void parameters (a) linear traverse method (b) modified point count method

2.8.2 Theory of Calculating Air Void Parameters

In both BS EN 480-11 and ASTM C457 standards, there is a step by step method in determining the air void parameters in hardened concrete. For these standards there are several equations that determine the air void parameters. In order to determine these parameters, initial values must be calculated which are given in Table 2.11.

Table 2.11 Initial air void parameter calculations to BS EN 480-11 and ASTM C457

Parameter	Definition	Calculation
BS EN 480-11		
T_s	Total length of traverse across solid phases	-
T_a	Total length of traverse across air phases	-
P	Paste content by volume calculated from the mix proportions	-
Ci	The number of individual chords across air voids in the various size classes	-
ASTM C457		
T_t	Total length of traverse	Sum of P_i x R_i
T_a	Traverse length through air	P_a x R_a
T_p	Traverse length through paste	P_p x R_p

Where:

P_i = pitch of the corresponding lead,
R_i = number of rotations of the respective lead screws, and
N = total number of air voids intersected

Using the initial values determined from the equation in Table 2.11, the user can then use the values to determine the air void parameters which are both detailed in BS EN 480-11 and ASTM C457. Table 2.12 outlines those equations in both standards in the order they would be used to calculate the parameters. There is a drawback to these standards. When the parameters are being calculated it is important to ensure that the initial results produced are correct otherwise there is a domini effect of inaccurate results that would affect the outcome.

Table 2.12 List of air void parameters, their definitions and equations used from BS EN 480-11 and ASTM C457

Parameter	Definition	Calculation		Size Range
		BS EN 480-11	ASTM C457	
Total traverse length (T_t), mm	Total length which the microscope moved over the sample.	$T_s + T_a$	$\sum P_i \times R_i$	Min. 2400mm
Total air content (A), %	Total amount of air calculated to be in the concrete whether entrained or entrapped.	$\frac{T_a \times 100}{T_{tot}}$	$\frac{T_a \times 100}{T_t}$	4-8%
Total number of chords measured (N), no.	Total number of air voids counted during the tested.	$\sum C_i$	nd	nd
Void frequency[1] (n), mm[2]	The number of voids intercepted by a traverse line – voids per unit length of traverse.	$\frac{\pi \times (5 + \ell_{max} - \ell_{min}) \times (\ell_{max} + \ell_{min})}{4 \times 10^6}$	$\frac{N}{T_t}$	nd
Average chord length ($\bar{l}$), mm	The average void size determined for the entire sample	nd	$\frac{T_a}{N}$ or $\frac{A}{100n}$	nd
Specific surface (α), mm^{-1}	The total area of the air voids divided by the volume	$\frac{4N}{T_a}$	$\frac{4N}{T_a}$ or $\frac{4}{\bar{l}}$	nd
Paste content (p), %	The percentage of the total volume of concrete which is just cement paste	nd	$\frac{T_p \times 100}{T_t}$	nd
Paste-air ratio (R), no.	The ratio of the total volume of the concrete and the total volume of air voids	$\frac{P}{A}$	$\frac{T_p}{T_a}$	nd
Micro-air content (A_{300}), %	The total air content of air voids 300µm diameter or less	Total air content to 300µm void diameter	nd	A_0-A_{300}
Spacing Factor[2] ($\bar{L}$), mm	The maximum distance between two air voids in the cement paste	When R is less than or equal to 4.342	$\frac{T_p}{4N}$	Max. 250µm
		When R is greater than 4.342	$\frac{3}{\alpha}\left[1.4\left(1+\frac{p}{A}\right)^{1/3} - 1\right]$	

[1]ℓ_{max} and ℓ_{min} are the maximum and minimum chord lengths within the class

[2]The spacing factor is determined using the same equation in both standards

nd – no data

2.8.3 The Use of Automated Air Void Analysis to Determine the Air Void Characteristics of Concrete

Automated air void analysis is a relatively new method which has only been properly optimized in recent years. The use of automated analysis was to not only speed up the analysis time (from 4-6 hours down to approximately 20-30 mins) but to increase the accuracy of the results (Elsen, 2001). Two standards are used to analyse the air void structure of a specimen. ASTM C 457 Part 9 (ASTM, 2012) is the American standard, EN 480 Part 11 (BSi, 2005) is the European standard, Table 2.13. The experiment itself consisted of using nine samples which were tested in all thirteen laboratories. The results for the experiment are shown in Table 2.14.

Table 2.13 Comparison between BS EN 480-11 and ASTM C457-09 (Elsen, 2001)

PARAMETER	**BS EN 480-11**	**ASTM C457-09**
Method	Linear-traverse method	A: linear-traverse method B: modified point-count method
Area	150 mm^2	155 mm^2
Number of specimens	2	≥ 1
Length of traverse line	≥ 2400 mm	≥ 2540 mm
Magnification of the microscope	100x ± 10x	50x to about 125x
Air void size distribution	Yes	No
Micro air content	Yes	No

Table 2.14 Results of the air content of hardened concrete using different analytical techniques (Elsen, 2001)

Laboratory	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Method	A	R	P	A	A	R	R	P	P	R	A	A	A
Specimen *Air content (vol. %)*													
1	2.4	2.6	3.1	3.6	2.5	3.0	3.0	3.4	2.6	1.7	2.3	2.9	2.5
2	3.9	3.9	3.9	4.8	3.5	4.0	4.0	3.9	3.1	2.7	4.5	3.2	3.7
3	12.3	11.1	13.0	13.1	14.2	8.8	13.8	12.1	11.8	10.3	13.4	13.8	11.4
4	0.9	1.5	1.7	1.1	1.3	1.5	1.3	1.6	1.0	1.2	1.2	1.9	1.1
5	7.9	7.9	9.7	9.6	8.6	8.1	9.3	9.1	7.8	6.4	9.8	7.7	8.4
6	4.8	4.9	4.6	5.7	4.8	4.7	5.4	6.9	3.9	3.5	5.8	5.8	5.3
7	8.9	7.3	6.2	6.8	9.1	5.9	9.3	9.1	10.1	6.9	8.3	9.3	8.6
8	9.0	8.3	9.5	7.9	9.4	7.0	9.1	9.0	9.3	8.5	8.6	8.5	8.2
9	1.3	1.0	0.9	1.0	1.3	1.4	1.6	1.5	1.6	1.0	1.2	1.4	1.4

A – Automated; P – Manual point count; R – Manual linear traverse (Rosiwal)

As the results show, there are large variations different methods are used to analyse the air content with large differences occurring when the same specimen is analysed by various methods (Elsen, 2001; Pleau, et al., 2001). For example, specimen 3, when analysed by laboratory C5 (automated) and C6 (manual linear traverse) saw a difference of 38% but when the two results are compared to laboratory C8 the results vary by 15% and 27% respectively insinuating that automated and manual point count are the better methods. Though that statement can only be made if other laboratories had similar results which in this study they do not meaning that human error has to be considered, so it is up to the user, how the results are interpreted and how the specimens are prepared.

Using automated analysis is found to be a more suitable option but problems do arise that have to be brought to attention. It was found that concretes that have porous aggregates contribute to the total air content (Elsen, 2001; Pleau, et al., 2001; Jakobsen, et al., 2006; The Concrete Society, 2014), but overall the advantages outweighed the disadvantages with the problem of human error being eliminated from the process so the results collected can be considered to be more accurate (Pleau, et al., 2001; Zalocha & Kasperkiewicz, 2005; Jakobsen, et al., 2006). Though Table 2.13 and Table 2.14 compare standards and analytical methods, it is hard to determine which method is best. Table 2.15 outlines the advantages and disadvantages of the various methods used for air void analysis.

Table 2.15 Advantages and disadvantages of the linear traverse method by manual and automated methods

Linear Traverse	**Advantages**	**Disadvantages**
Manual	- Focus on a particular area can be analysed fully by the operator. - Scope focus can be adjusted if surface is uneven.	- Each slice requires 6 hours to analysis fully - Polishing the samples requires 4 different grades of grit for the required smoothness. - Large space for human error.
Automated	- Approximately 20 mins to scan a concrete slice compared to 6 hours for the manual methods. - 95% accuracy rate when hardened air content is compared to the fresh air content. - Parameters between ASTM and BSi can be changed easily.	- Preparation takes 1 hour for each slice and for the test method 2 slices are required. - Test surface must be very smooth for the equipment to read the surface correctly. - Cannot distinguish between entrained and entrapped air.

2.9 Preventing Further Ice Build-up Through the Use of De-icing Agents

In the UK, grit spreading on roads and pavements are determined based on the weather forecast and the volume of traffic travelling on a stretch of road. Moreover, specific salt is used depending on the type of road. Table 2.16 shows the type of salt available for each weather possibility and the flow of traffic. This table has been manipulated from a document endorsed by the Department of Transport (Roads Liason Group, 2013). Typically, a gritter would spread 20g of grit salt over every m^2 of surface and this is done twice a day (DCC, 2017). For the rest of Scotland, each council outline specifications for their public roads and pathways whilst Transport Scotland have outlined guidelines for all trunk roads in Scotland (Each of the freeze-thaw classes above provide a basic description on when various concretes designs should be considered. The four descriptions are based on how saturated the concrete is and whether there is de-icing salt or sea water present. This is not enough to protect the concrete against freeze-thaw attack; thus, a fifth class should be added for the more extreme and realistic conditions which concrete is subjected to.

Table 2.17). On the gritting routes, pre-wetted salt is used which is a mixture of dry (marine) salt and fully saturated brine salt in in a 70:30 respectively, creating a concentration of approximately 23% (Transport Scotland, 2018).

Table 2.16 Dundee City Council figures for the spread of grit salt over an area for a particular salt, weather condition and volume of traffic on a road and pavement (DCC, 2017)

Salt Type[1]	**Precautionary Treatments Before Snow or Freezing Rain**	**Spreading, g/m²**	
		Light or Medium Traffic	**Heavy Traffic**
Dry Salt	Light Snow Forecast	20	20
Pre-wet Salt		20	20
Treated Salt		15	15
Dry Salt	Moderate/Heavy Snow Forecast	20	40
Pre-wet Salt		20	40
Treated Salt		15	30
Dry Salt	Freezing rain Forecast	1 x 20 then monitor	
Pre-wet Salt		1 x 20 then monitor	
Treated Salt		1 x 15 then monitor	

[1]Type of salt used is marine salt in accordance with BS 3247 (BSi, 2011b) in the Dundee City area which is imported from countries with warm climates. The salt consists of calcium sulphate and magnesium chloride with minor insoluble material.

Each of the freeze-thaw classes above provide a basic description on when various concretes designs should be considered. The four descriptions are based on how saturated the concrete is and whether there is de-icing salt or sea water present. This is not enough to protect the concrete against freeze-thaw attack; thus, a fifth class should be added for the more extreme and realistic conditions which concrete is subjected to.

Table 2.17 Transport Scotland figures for the spreading of grit salt (Transport Scotland, 2018)

Salt Type	**Precautionary Treatments Before Snow and Freezing Rain**	**No. of precautionary treatment routes**	**Spreading, g/m^2**
Pre-wetted salt	Snow forecast	92	20
	Snowstorm forecast	107	40

Winter conditions in the UK see the temperatures drop below 0°C freezing surface water and turning into ice. Ice on roads causes treacherous condition for the road users so the implementing of de-icing salt reduces and prevents this from happening. De-icing salt works by lowering the freezing point of water. This is dependent on the amount of salt and type of salt used. There are a range of de-icing salts available (Table 2.18) depending on the use, for example, NaCl can be used on roads and pavements but not bridges as this would corrode the steel. Instead, Urea is used on bridges. Each salt available has a eutectic point where a particular temperature reached, and the salt is unable to melt the ice.

Table 2.18 Various de-icing agents available and their respective eutectic temperature points (Achkeeva, et al., 2015)

De-icier	**Symbol**	**Eutectic Point, °C**
Inorganic salts		
Sodium chloride	$NaCl$	-21.2
Magnesium chloride	$MgCl_2$	-33.6
Calcium chloride	$CaCl_2$	-49.8
Potassium chloride	KCl	-10.6
Organic salts		
Calcium magnesium acetate	$CaMg_2(CH_3COO)_6$	-27.5
Potassium acetate	KCH_3COO	-60.0
Potassium formate	$KCHOO$	-55.0
Sodium formate	$NaHCOO$	-16.0
Urea	$CO(NH_2)_2$	nd
nd – no data		

2.10 Development and Implementation of Standards for Freeze-Thaw Attack

2.10.1 Background

The development of the standards for specifying concrete have been an ongoing process for decades with major changes occurring more recently (Table 2.19). These major changes include the implementation of Exposure Classes and then relating them to the concrete properties including the water/cement ratio, cement content, compressive strength and cover depth (Concrete Society, 1999). Since the incorporation of BS EN 206 in 2003 there have not been any major changes. The exposure conditions are divided into six classifications that are defined by the deterioration mechanism as shown in Table 2.20.

Table 2.19 Summary of changes in British Codes development (Concrete Society, 1999; Newlands, 2001)

	1950/57 CP114	**1959 CP115**	**1965 CP116**	**1972 CP110**	**1985 BS8110**	**1997 BS5328**	**2003 EN206**
No. of Exposure Conditions	2	2	7	5	5	6	18
Concrete Property linked to Exposure Condition							
Concrete Grade	✗	✗	✓	✓	✓	✓	✓
Min. Cement Content	✗	✗	✗	✓	✓	✓	✓
Max. w/c ratio	✗	✗	✗	✓	✓	✓	✓
Cover	✓	✓	✓	✓	✓	✗(1)	✗(1)

(1)Covers specified in appropriate design standard

Table 2.20 Exposure classifications defined in BS EN 206 (Newlands, 2001; BSi, 2013a)

Exposure Class	Deterioration Mechanism	Example
X0	No risk of corrosion or attack	Concrete inside buildings with low humidity
XC	Corrosion induced by carbonation	Majority of exposed concrete surfaces
XD	Corrosion induced by chlorides other than from sea water	Swimming pools, car park slabs, bridges
XS	Corrosion induced by chlorides from sea water	Coastal structures, parts of marine structures
XF	Freeze-thaw attack with or without de-icing agents	Road and bridge deck, splash zones of marine structures exposed to freezing
XA	Chemical attack	Foundations, tunnel linings, industrial floors

As this project is concerning with mainly freeze-thaw attack, only Class XF will be examined in more detail (BSi, 2013a):

Class XF1 – Moderate water saturation, without de-icing agent

This class is designated for concrete which is exposed to the wet environment including vertical surfaces that are not highly saturated but are subjected to rain and freezing. Though the likelihood that concrete is subjected to deterioration is minimal due to a high degree of saturation. Examples of these subjected to this class are columns and facades.

Class XF2 – Moderate water saturation, with de-icing agent

Class XF2 details concrete in an environment that is exposed to wet conditions as stipulated in XF1 though with the addition of airborne de-icing salts. Minor ingress of chlorides from the de-icing salts due to moderate saturation. Examples include those described in XF1 and surfaces on parts of bridges but are exposed to de-icing salts directly or from run-off.

Class XF3 – High water saturation, without de-icing agent

This classification is designated to horizontal concrete surfaces that are subjected to very wet environments and is of high significance in freeze-thaw attack. XF3 exposure conditions require a high saturation level to initiate the freeze-thaw scaling commonly seen in wet/cold climates. Examples of this class include those described in XF1 but under constant splashing and exposure to freezing conditions.

Class XF4 – High water saturation, with de-icing agent or sea water

As with the classification XF3, Class XF4 groups together conditions to which concrete is subjected to high saturation with the addition of de-icing salts. This class is more pertaining to the UK climate as the UK is characterized as a cold/wet climate due to the low temperatures and high precipitation rates. Examples include horizontal concrete surfaces such as roads and pavements and splash zones of marine structures.

2.10.2 Recommendations for Concrete in BS EN 206 for XF Exposure Class

In comparison to previous documents, BS EN 206 has nominated to be a performance-based specification for concretes. It recommends specific concretes to a specific concrete exposure class selecting concrete properties suitable for performance. Table 2.21 outlines concrete properties recommended in BS EN 206 for exposure class XF. The values given in Table are based on the following assumptions:

a) The values given are intended for a structure with a working life of 50 years.
b) The common cements used must conform to BS EN 197-1: 2011 (BSi, 2011a) with a nominal aggregate size of 20 – 32 mm.

Many cement types have been excluded from BS EN 206 as each country has access to various cements. Cement combination as explained in BS EN 197-1 are further detailed in each European country' supplementary standard.

Table 2.21 Recommended limiting values for composition and properties of concrete for and intended working life of 50 years in BS EN 206.

	Freeze-Thaw Exposure Class			
	XF1	**XF2**	**XF3**	**XF4**
Maximum w/c ratio	0.55	0.55	0.50	0.45
Minimum Strength Class	C30/37	C25/30	C30/37	C30/37
Minimum Cement Content[(1)] (kg/m^3)	300	300	320	340
Minimum Air Content (%)	-	4.0	4.0	4.0

[(1)] Cement type CEM I is used in accordance with BS EN 197-1

NOTE: Concrete subjected to freeze-thaw is required to have aggregates capable of resisting freeze-thaw attack in accordance with EN 12620

2.10.3 Recommendations for Concrete in BS 8500 for Exposure Class XF

BS 8500 is the complementary standard to BS EN 206 whereby it is more tailored to the country's requirements allowing for a more detailed specification. Though BS 8500 must be used in conjunction with BS EN 206 it is considered to be, in a way, guidelines for BS 8500 allowing for the specifier to design to the supplementary standard but being required to be cross checked with BS EN 206. Table 2.22 describes the limiting values for composition and properties for exposure class XF in BS 8500. Since BS 8500 is more commonly used in the UK than BS EN 206 there are several differences between the two standards which include:

a) Further diversification of the minimum strength class used. BS EN 206 only stipulated one strength class to be used whereas BS 8500 defines three in conjunction with cement content and air content.
b) Water/cement ratio varies depending on minimum strength class chosen and whether there is a requirement for air entrainment.
c) Total air content varies on the size of the aggregates used.
d) BS 8500 allows for cement combinations to be used rather than the standard CEM I recommended in BS EN 206.

Table 2.22 Limiting values for composition and properties of concrete to resist freezing and thawing XF exposures (BSi, 2015a)

Exposure Class	Min. Strength Class	Max. w/c ratio	Min. air content (%) and min. cement or combination content (kg/m^3) for max. aggregate size				Other requirements	Cement and combinations
			32 mm or 40 mm	20 mm	14 mm	10 mm		
XF1	C25/30	0.60	4.0	4.5	5.5	6.5	-	See(1)
			260	280	300	320		
	C28/35 LC28/31	0.60	-	-	-	-		
			260	280	300	320		
XF2	C25/30	0.60	4.0	4.5	5.5	6.5	-	See(1)
			260	280	300	320		
	C32/40 LC32/35	0.55	-	-	-	-		
			280	300	320	340		
XF3	C25/30	0.60	4.0	4.5	5.5	6.5	Freeze-thaw resisting aggregates(3)	See(2)
			260	280	300	320		
	C40/50 LC40/44	0.45	-	-	-	-		
			320	340	360	360		
XF4	C28/35	0.55	4.0	4.5	5.5	6.5	Freeze-thaw resisting aggregates(3)	See(2)
			280	300	320	340		
	C40/50 LC40/44	0.45	-	-	-	-		
			320	340	360	360		

(1) CEM I, II/A-D, II/A-L, II/A-LL, II/A-S, II/B-S, II/A-V, II/B-V, III/A, III/B, IVB-V

(2) IVB-V is not used for XF3/4 as the limiting factors for fly ash and GGBS is 35% and 55% respectively

(3) In accordance with EN 12620

The standards provide design guidance for various deterioration mechanisms but do not provide enough detail as to protect the concrete. BS EN 206 and the more specific BS 8500 provides options for durability. However, this in itself is a problem. BS EN 206 gives a description on which class is suitable for each scenario, but this is not country specific such as BS 8500. The exposure classes described do not include and XF5, hence, BS 8500 does not provide details on how to design for extreme weather and extreme preventive measures (i.e. multiple applications of de-icing salt).

Moreover, testing for these conditions is difficult due to the number of parameters involved in the freeze-thaw test method (CEN/TS 12390-9) which is based on the Swedish freeze-thaw test where Sweden's temperatures are far harsher than the UK. This means that concrete is being tested for conditions that very rarely occur.

BS 8500 provides minimum design strengths as well as cement and air content when designing for freeze-thaw durability. The standards also provide the option whether to increase the design strength or to reduce the design strength but add in air entrainer. Though both these options are viable for durability it still does not provide complete protection as deterioration still occurs. With the addition of XF5, concrete would require not only require a higher strength, for example C40/50, but a necessity to include air entrainer ensuring full protection.

In addition to concrete being higher strength or having air entrainer, lightweight concrete which is concrete that uses lightweight aggregates rather than conventional normal weight aggregates. This concrete is a third option in the standards that can withstand freeze-thaw attack. Normally, concrete that is highly saturated is subjected to freeze-thaw (XF3 and XF4) it would require freeze-thaw resisting aggregates such as granite that have a higher density to increase the concrete's performance because porous aggregates (gravel) tend to not be able to resist the expansion of ice. However, lightweight aggregate is a strange material in a way that it's a very porous material having a high-water absorption value (14%) yet it can withstand the harsh testing regime.

2.10.4 Test Methods for Concrete Subjected to Freeze-Thaw Attack

Freeze-thaw attack has been shown to create a wide range of problems regarding concrete damage and subsequently causing a review on how the concrete is designed to resist freeze-thaw attack. One of the current issues with understanding the mechanisms for freeze-thaw and salt scaling is how to properly test for freeze-thaw and salt scaling. Freeze-thaw attack is proven to be a big problem and to combat this testing has been devised to design concrete to resist this attack. From this several testing procedures were devised to properly design and test against freeze-thaw.

2.10.4.1 British/European Method (CEN)

In accordance with BS EN 206, BS EN 934 Part 2 (BSi, 2009b) specifies that for concrete to have the capability to withstand freeze-thaw, the air content has to be between 4% and 6% with a minimum content of 2.5%. Furthermore, there is also a requirement that the concrete has a compressive strength greater than/equal to 75% of the control (meaning the mix without air entrainment) after 28 days of curing. With these parameters specified, it is then possible to test the concrete against freeze-thaw resistance as outlined in BS EN 12390 Part 9 (BSi, 2016).

The test procedure involves subjecting the concrete samples to freezing and thawing in a saline solution, in a typical 24-hour cycle. For the first 16 hours of the cycle the concrete goes through the freezing process reaching temperatures of -18°C ± 3°C followed by a thawing stage lasting a period of 8 hours whereby the temperatures reach 20°C ± 3°C. Figure 2.20 depicts the temperature range envelope to which the concrete specimen is subjected to the freeze-thaw process.

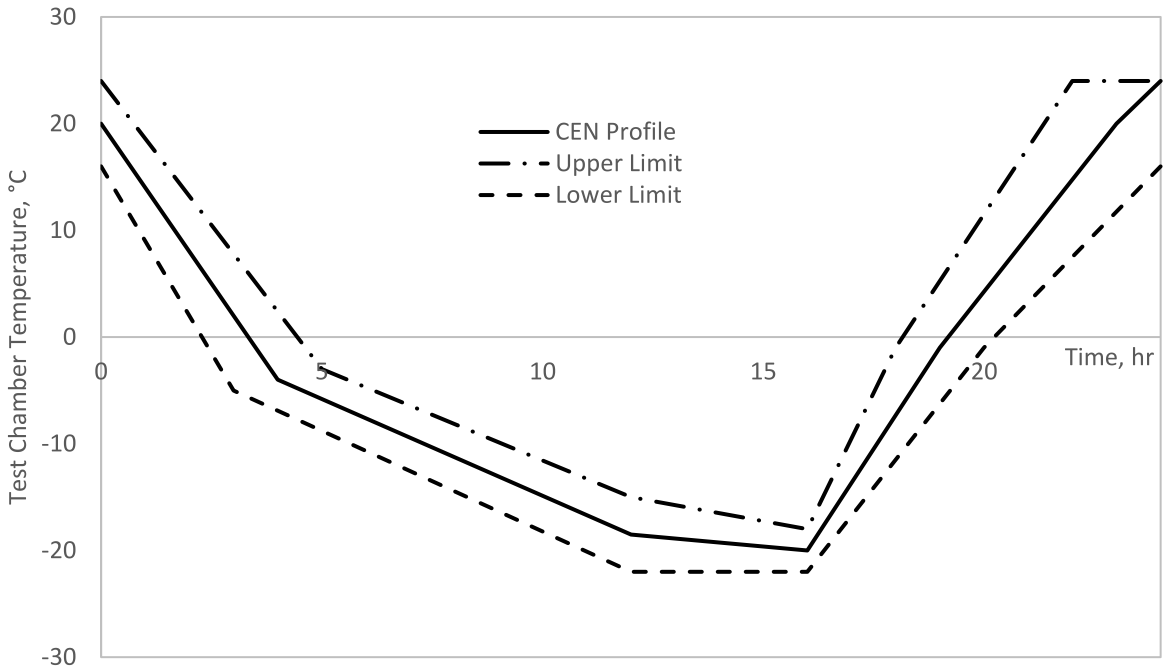


Figure 2.20 Freeze-thaw temperature envelope for CEN/TS 12390-9 freeze-thaw test method (BSi, 2016)

The freeze-thaw process runs (typically) for a total 56 cycles and at the end of the test the total accumulated scaled material is weighed to determine the significance of the freeze-thaw.

2.10.4.2 American Method (ASTM)

Testing freeze-thaw in America is done in accordance to the ASTM C 666/C 666M-08 standard, "Resistance of Concrete to Rapid Freezing and Thawing" (ASTM, 2008). The test procedure entails subjecting concrete beams to either, rapid freezing and thawing in water (Procedure A) or, rapid freezing in air and thawing in water (Procedure B). During the test, the temperature varies between 4°C to -18°C in the freezing stage then -18°C to 4°C during thawing, and this process occurs between 2 to 5 hours (Figure 2.21). Furthermore, it is a requirement that at the centre of the specimens and at the concrete surface, the temperature shall not exceed 28°C (ASTM, 2008).

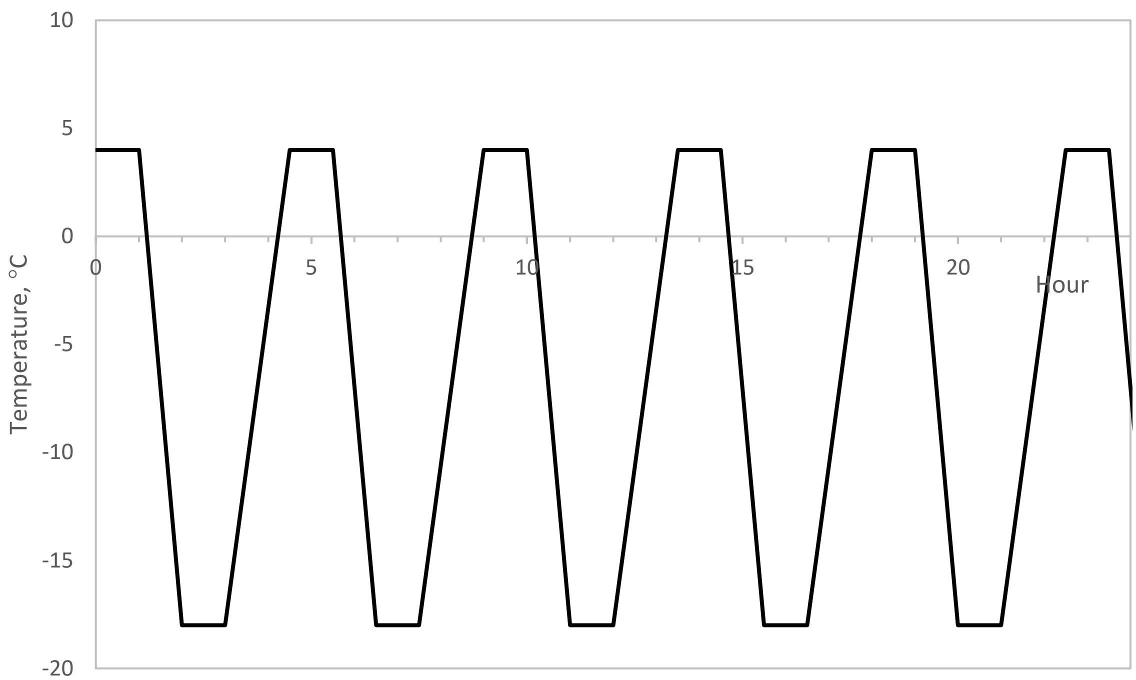


Figure 2.21 Temperature profile for a 24 hour cycle (ASTM, 2008)

2.10.4.3 Russia Method (GOST)

Freeze-thaw testing in Russia is undertaken in accordance with GOST 10060:2012, 'Method for the determination of frost resistance'. The test method includes freezing and thawing the concrete samples in a short duration, where a single cycle can take up to 6.5 hours to complete allowing for just over 3 cycles to be complete in 24 hours. Out of all the freeze-thaw test methods, GOST has the highest salt concentration of 5%.

2.10.4.4 Chinese Method (GB/T)

The Chinese method for freeze-thaw is done in accordance with GB/T 50082:2009 standard, 'Standard for test methods of long-term performance and durability of ordinary concrete'. The test involves concrete cuboids subjected to two cycles every 24 hours with a temperature range of +20°C to -20°C. Like the ASTM test method, the Chinese method includes testing the dynamic modulus of elasticity and measuring the weight loss. This test method appears to be a combination of the CEM and ASTM test methods for freeze-thaw whereby both the dynamic modulus and the mass loss due to scaling are both measured during the test.

Completing the test is dependent on three different conditions which need to be meet; the test method reaches 28 cycles (equate to 16 days of testing), the mass loss of scaled material reaches 1.5kg/m^2 or the dynamic modulus drops below 80%. This test has a shorter duration compared to the other freeze-thaw testing procedures which indicates that the concrete is not being fully tested for durability. All the test methods described above are shown in Table 2.23.

Table 2.23 Comparison of freeze-thaw test methods in different countries

Parameter	CEN (British/European)	ASTM (American)	GOST (Russian)	GB/T (Chinese)
Standard Notation	12390-9:2016	C666:2008	10060:2012	50082:2009
Temperature profile	(+23°C, -18°C)	(+4°C, -18°C)	(+20°C, -18°C)	+20, -20
Salt concentration	3%	0%	5%	3%
No. of cycles in 24 hrs	1	4.33	3.69	2
Carbonated	No	No	No	No
Dimensions of sample	150x150x50mm	400x75x75mm	150x150x150mm	150x150x150mm

2.11 Problems with CEN/TS 12390-9 Freeze-Thaw Test Method

The freeze-thaw test method provides a rough estimation on how the concrete would endure the freezing winter temperatures. But it's not without its flaw. The test is built off the Swedish test method for freeze-thaw where the concrete is subjected to very low temperatures which provides a good approximation on how durable the concrete is. In the UK it is rare that the temperature would reach that level. It is noted that in the past the temperatures have been below -10°C but not enough to use the temperature profile as detailed in CEN/TS 12390-9 which is limited to -24°C.

Moreover, there are a few flaws in the scaling test itself. The saline solution has a fixed salt concentration of 3% which is not a good representation of the real world since multiple layers are added every day to prevent ice forming. Removing the scaled material by means of a brush means the material to flick off and become lost affecting the final result. The glue used to stick the rubber round the outside of the sample contracts when the temperature drops causing the glue to pull off the surface concrete.

Other problems the scaled material on the sides and base of the sample which are not considered. Many samples lose materials from these parts and if the result was adjusted to account for this loss then it may be seen that the sample fails rather than passes. Furthermore, the test surface is the central slice of the sample which has been discussed (Kreijger, 1990) to be of better quality than the cast surface, though it is the cast surface which is subjected to salt scaling so the test should take this into consideration.

2.12 Summary of Literature Review

The review of the past and current literature highlight that temperatures have varied significantly over the years and while the temperatures are constantly in flux, they are not as harsh as they were a decade ago (The Met Office, 2015). However, it should be noted that there are occasions during the winter months where temperatures have dropped below freezing and adequate protection has not been achieved.

Currently, there are sustainability agendas which are outlining the use of more sustainable materials rather than CEM I. Not only will this reduce the CO_2 levels entering the atmosphere from concrete processes, but it will also reduce waste from other industries such as coal burning for energy and smelting as the by-products from these types of industries can be used to replace CEM I content by a considerable percentage. The use of said materials have several factors which influence the microstructural properties, thus, the freeze-thaw durability of concrete containing replacement materials.

Nowadays, there is a vast range of admixtures available and have become commonplace in concrete and mortar. Established performance in CEM I concretes show that these admixtures aid in any situation, however, their mechanisms in other materials such as CEM II/B-V, CEM III/A, CEM II/A-L and CEM II-V are less well known. Furthermore, using admixtures to aid in the durability aspects such as freeze-thaw is a necessity but, using these admixtures with replacement materials is more difficult as admixture like AE tend to be designed for CEM I concretes only. Moreover, it is also difficult to determine how the cement paste reacts with two or more different admixtures coupled with replacement material.

Freeze-thaw attack mainly falls into two mechanisms: internal freeze-thaw and freeze-thaw salt scaling. Both have a few different theoretical mechanisms although there is no agreement on the specific cause of freeze-thaw damage. Internal freeze-thaw mechanisms such as hydraulic pressure (Powers, 1945), crystallization pressure (Helmuth, 1962) and osmotic pressure (Powers, 1975) have been used to try and explain the internal workings during freeze-thaw attack. Freeze-thaw salt scaling mechanisms such as thermal shock (Mather, 1979), precipitation and growth of salt (Weissenberger, et al., 1992), salt concentration (Binda & Baronio, 1987), glue spalling (Valenza & Scherer, 2006) have been theorized to as to what causes the material loss from the surface. Both internal freeze-thaw and salt scaling are linked in a way as each theory requires another to fully deteriorate the concrete.

It is revealed that air entrainment plays a pivotal role in the durability of concrete during freezing and thawing conditions. However, understanding why the microstructure acts the way it does is a difficult problem. Ideally the air bubbles from air entrainment should be single sized and distributed evenly throughout the concrete but this is not the case. Powers (1945) suggested that a spacing factor of 250 μm (0.25mm) or less is suitable to prevent freeze-thaw damage. But later this was reduced by Backstorm *et al.*

(1958) who showed that a spacing factor should be between 100 and 200 µm (0.10-0.20mm) in rapid freeze/thaw tests. This led to the critical spacing factor, as those of Powers and Backstorm are reliant on knowing the moisture content of concrete. Fagerlund (1993) identified that the true critical spacing factor may be as high as 300µm (0.30mm) and depends on the freezing medium (water or salt water).

Even though it has been determined that a spacing factor limit of 200 µm would provide enough protection for the concrete, there are other factors which must be considered when designing concrete, namely, the influence of cement types. Various cement types are used to replace a certain percentage of CEM I, but it is difficult to identify how they influence air void formation. CEM I tends to be the easiest to entrain air as most air entrainers are designed for this type of cement. The viscosity of the cement prevents the entrained air bubbles from escaping or coalescing as the material acts like a cushion (Du & Folliard, 2005).

CEM II concretes are known to have issues when it comes to entraining air in the concrete as the unburnt carbon absorbs the admixture reducing the resistance concrete has to freeze-thaw (Gebler & Klieger, 1983). When fly ash does become air entrained it has been reported that there are issues when it comes to transporting and handling (Zhang, 1996) and a loss of air over time (Kulaots, et al., 2003).

The inclusion of slag (CEM III/A) was found to cause disruption to the air void system in concrete even at low levels (30%). This led to an increase in spacing factor of around 100µm (0.10mm) and a reduction in specific surface by around 10-11mm^{-1} (Giergiczny et al, 2009).

New image analysis technology has allowed microstructural analysis to be conducted in a significantly reduced timeframe. These new techniques can rapidly assess air void parameters in concrete however, calibration is a prerequisite. Comparisons made between EN 480-11 and ASTM C457-9 regarding air void analysis show that EN 480-11 can determine the entrained air content and pore size distribution which are required to determine the air void characteristics regarding freeze-thaw durability.

Various cement types have been used in concrete each with different results when subjected to freeze-thaw attack. CEM I is seen to have a high resistance to freeze-thaw attack with a suitable air entrainment percentage and adequate strength. Higher strength with no entrainer has been seen to be as good as a concrete with low strength but a good air entrainment level (Du & Folliard, 2005).

CEM II/B-V has shown to reduce the freeze-thaw durability of concretes, and said durability diminishes when the replacement percentage increases (Zhang, et al., 1998). Durability of CEM II/B-V in freeze-thaw is in dispute due to several conflicting studies which do not diversify the difference between internal freeze-thaw damage and salt scaling. The use of various sources of CEM II/B-V (variable fineness, carbon content etc.) do not allow for a comparable comparison to be conducted as the properties vary quite significantly.

The effects of CEM III/A in freeze-thaw attack have been noted to have significant problems, especially in salt scaling. However, it was observed that with lower CEM III/A levels, the concretes have similar, if not, the same durability to CEM I (Stark & Ludwig, 1997). CEM III/A concrete subjected to freeze-thaw is seen to have a high initial mass loss but then minimal loss thereafter (Bijen, 1996). The inclusion of air entrainment is understood to have little to no affect in protecting the concrete as studies have shown that the total mass loss is the same for both air entrained and non-air entrained CEM III/A concretes. Carbonation of the surface of CEM III/A may be playing a role in exacerbating freeze-thaw attack (salt scaling) however the near surface mechanism is uncertain.

Chapter 3
Research Methodology, Materials and Test Methods

3.1 Introduction

The main objectives of the research project were to examine the practicality of freeze-thaw design and testing on a wide range of concretes and strengths and determine the causes of deterioration. In Chapter 2, many theories were analysed to obtain a reasoning behind the deterioration mechanisms that have shown to be problematic to concrete durability. According to BS8500, either the strength is increased, or air entrainment is added to the concrete mix design to increase a concrete's resistance to freeze-thaw attack. Different cementitious materials that are now available on the market do not have the same hardened properties to withstand the damaging effects of freeze-thaw. Furthermore, the 'off the shelf' admixtures designed to protect the concrete are an alternative option to reducing the water/cement ratio but according to BS8500 either option is suitable for XF exposure class.

The research also assessed the various aggregates that are available considering the freeze-thaw durability and how they respond when subjected to freeze-thaw action. Detailed investigation is done on lightweight aggregate, produced from compressing fly ash, as this material provides unusual characteristics when subjected to physical and chemical testing.

Determining the air void characteristics is a fundamental tool in investigating how the various concrete types respond to physical demand when the concrete is subjected to freeze-thaw attack. Moreover, it will also aid in determining how each of the cementitious materials available react to the various admixtures that are required to improve, prevent or help a concrete's performance.

With the move from conventional CEM I towards increased replacement materials, in an effort to reduce carbon footprint, there is also a necessity to consider the European test for freeze-thaw (CEN/TS 12390-9) in that the parameters laid out, such as the salt concentration, effect of carbonation and the temperature profile.

During the winter, roads and pavements tend to have ice form on the surface forcing authorities to spread de-icing salt for health and safety. Continual spreading of this material increases the concentration of the solution, thus the increase in the concentration of salt infiltrating the concrete. Each winter temperatures fluctuate describing the winter to be either mild or cold, with one occasional winter being very cold subjecting concrete to major freezing and thaw. The standard for testing the concrete (CEN/TS 12390-9) describes using a temperature profile that reaches a temperature of -18°C which is unrealistic for the UK. These parameters are only a couple which will be described in this chapter.

3.2 Experimental Programme

The experimental programme for the research project is shown in Figure 3.1.

Phase 0: Literature Review

An extensive literature review has been undertaken to (1) understand the main theories of freeze/thaw attack in concrete systems and the influence of the presence of de-icing salts, (2) assess the influence of admixtures (air entertainers and superplasticisers) and admixture compatibility on entrained air void characteristics, (3) determine the influence of constituent materials, including modern cement combinations on air void formation, (4) review the test methodologies available for assessing freeze/thaw resistance of concrete.

Phase 1a, 1b and 1c: Laboratory Study of BS8500 Concretes (including aggregate effects)

Phase 1a consists of a range of laboratory produced concretes tested over the duration of the project. These concretes have been designed to comply with BS8500, XF4 in terms of strength and air content requirements. Cement types tested include CEM I, CEM II/B-V, CEM III/AA, CEM III/AB and CEM II/A-L. Freeze-thaw testing to CEN/TS 12390-9 was carried out to determine the performance of different cement types and target strengths to create a baseline for data comparison. Furthermore, air void characteristics were assessed using automated image analysis equipment (RapidAir 3000). Work carried out has been using freeze-thaw resisting aggregates to BS8500 as well as aggregates that do not comply.

Phase 1b continues from Phase 1a by looking at the performance of the concrete during freeze-thaw after being subjected to carbonation. It has been considered that carbonation does play a role of the freeze-thaw performance so Phase 1b will investigate this. Furthermore, this phase will then tie in with varying the freeze-thaw test parameters in Phase 4.

Different aggregates, complying with BS8500 XF4 freeze-thaw resistance, were investigated in Phase 1a. However, lightweight aggregates have not been identified as to whether they are capable to withstand freeze-thaw. In Phase 1c, lightweight aggregates were subjected to various durability testing for both the aggregate itself and concrete containing lightweight aggregate.

Phase 2: Admixture Compatibility in Concretes

Air void characteristics will be influenced by the presence of other admixtures as well as their interaction with cement combinations. This is currently being examined using the EN480-11 against reference cements and admixture combinations and using automated air void analysis.

Phase 3: Performance of Representative UK Concretes to BS 8500-1

The work in Phase 3 consists of submitting a series of protocols to industry concrete producers where they would cast the desired concretes for testing. These concretes are a representation of what the selected producers would batch had the concrete been used on a construction site. This will then aid in determining how the concretes react when subjected to freeze-thaw. The concrete's designs are primarily based on what the producers would normally batch and the materials that they have available to them.

Phase 4: Changing F/T Scaling Test Method in CEN/TS 12390-9 to Suit the UK Climate

Phases 4 will focus on changing the parameters laid out in CEN/TS 12390-9. This will involve looking at varying the salt concentration of the solution placed on top of the sample for testing to represent the multiple applications of de-icer, thus, the increase in salt concentration during the winter months. The temperature profile of the test will be altered to make the test less harsh and more suitable for the UK and European climates. Tying in with the work done in Phase 1b, several concretes (each with the same target strength and either being air entrained or non-air entrained) have been subjected to accelerated carbonation before being test for freeze-thaw.

Phase 5: Guidance and recommendations for F/T environments

Once the previous phases have been completed and the data compiled and analysed, then suitable recommendation can then be considered as to whether the various cement types used during the course of the research project are suitable for concretes that have to undergo freeze-thaw, determine how much of an influence the microstructure of the concrete has on the durability to withstand freeze-thaw and how varying the parameters of the freeze-thaw test method for a more suited regime can provide a better representation of concrete in the real world.

3.3 Material Characteristics

The chemical and physical attributes for all materials used for this project were tested by the author. The particle size distribution for the fine cementitious material was tested six times (by the author) and an average was taken.

3.3.1 Portland Cement (CEM I)

The CEM I used throughout the research was sourced from a single manufacturer, Hanson Cement Group, conforming with BS EN 197-1 – Grade 52.5N was used (BSi, 2011a). The cement was stored in airtight containers preventing an ingress of moisture causing the cement to harden. The chemical and physical properties are shown in Table 3.1 and Figure 3.2 respectively.

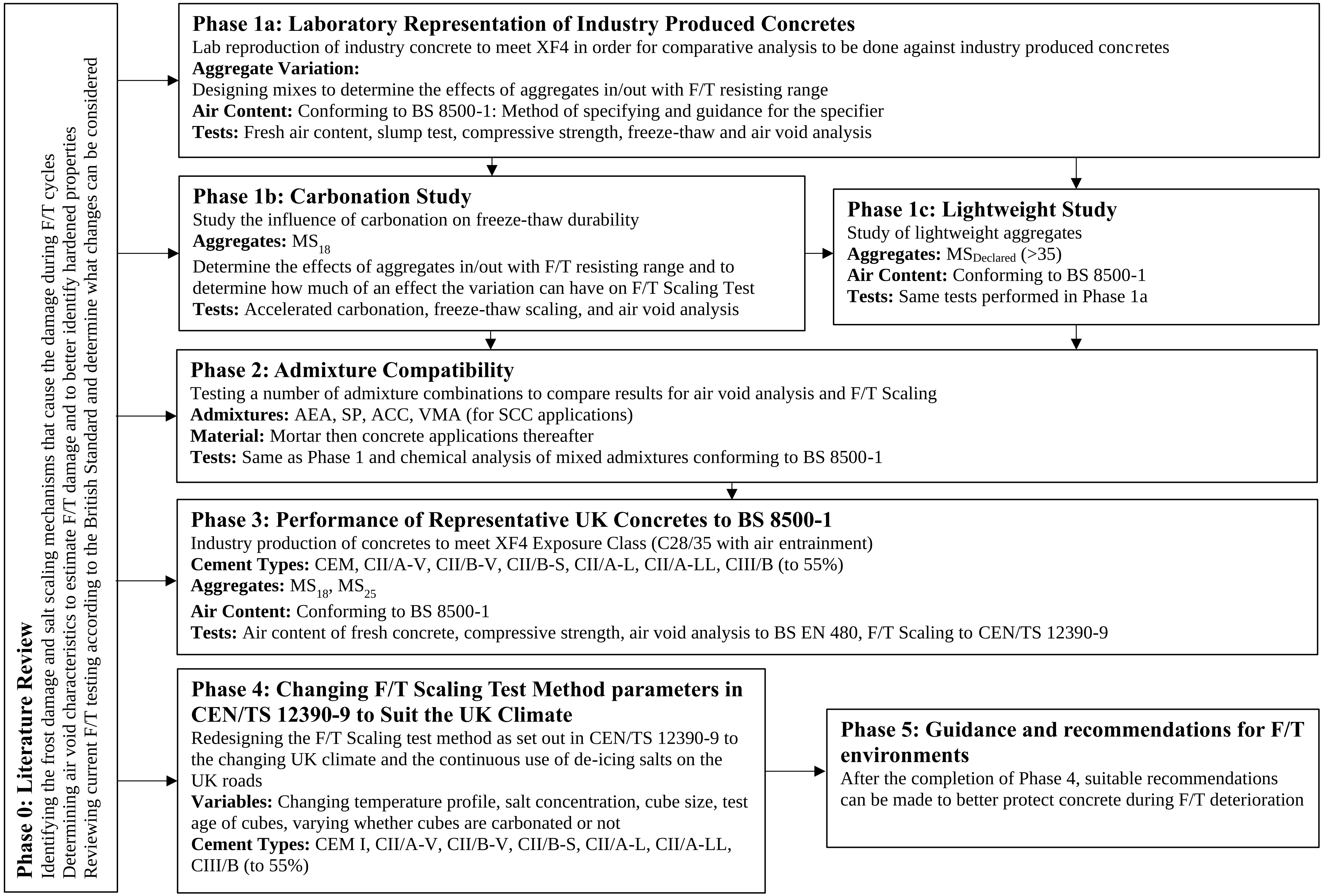


Figure 3.1 Experimental programme

3.3.2 Fly Ash (FA)

Five different fly ashes were used in the project all complying with BS EN 450 Part 1 (BSi, 2012). One type of fly ash (DFA 1) was used as a reference bulk whilst the rest were used in comparison. The bulk fly ash properties are shown in Table 3.1 and

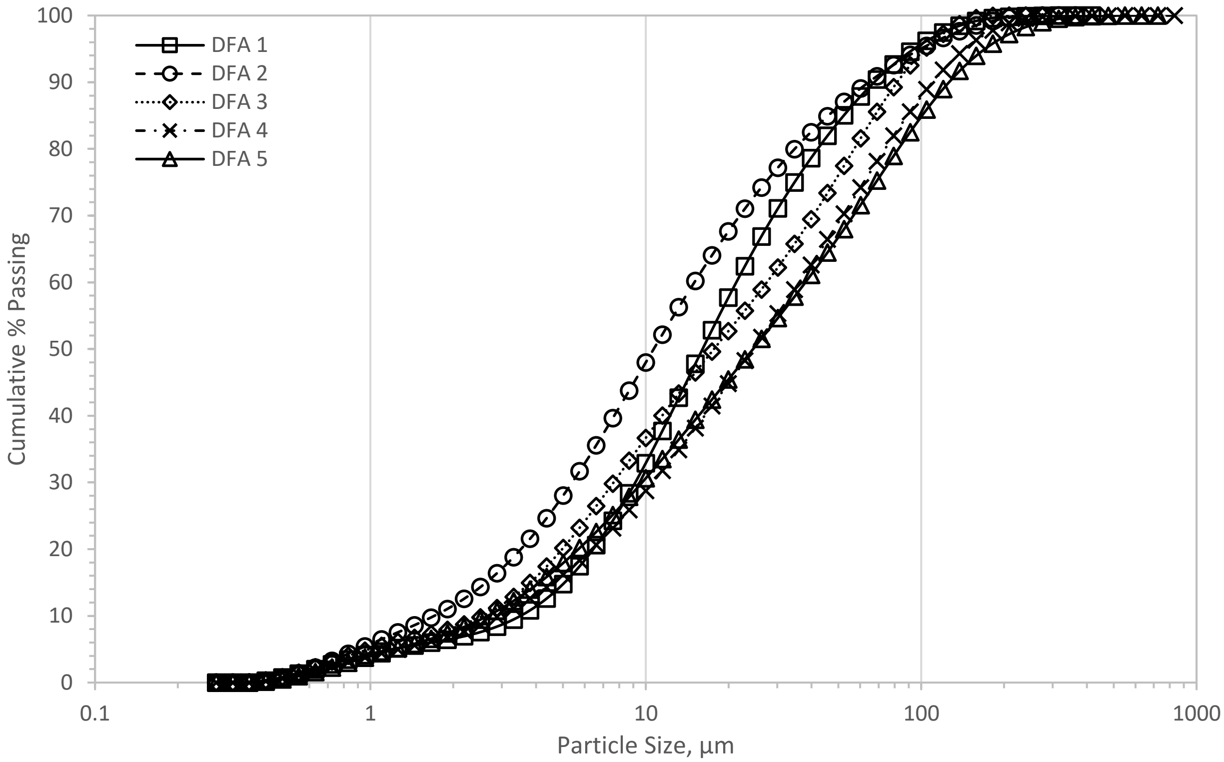


Figure 3.3. The remaining fly ashes' chemical and physical properties are given in Table 3.1 and

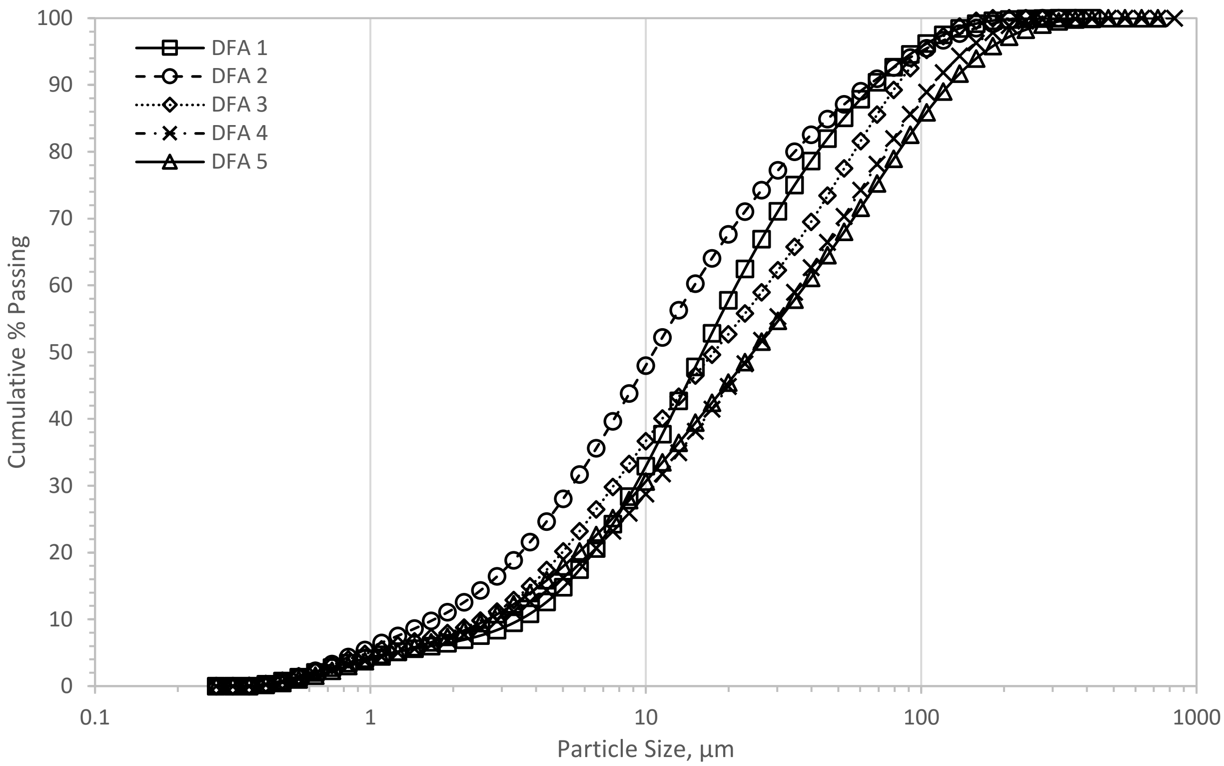


Figure 3.3 respectively.

3.3.3 Ground Granulated Blast Furnace Slag (GGBS)

A single bulk source of GGBS was used during the research. The material was supplied in airtight containers from Hanson Cement Group conforming to BS EN 15167 Part 1. Both the chemical and physical properties are shown in Table 3.1 and Figure 3.2.

3.3.4 Limestone Fines (LS)

The limestone used was crushed calcium carbonate limestone conforming to BS 7979 (BSi, 2016). The chemical and physical properties are shown in Table 3.1 and Figure 3.2.

3.3.5 Coarse Aggregate

Three types of aggregate; crushed granite, locally sourced natural gravel and lightweight aggregate were used in the project conforming to BS EN 12620:2002. The aggregates included crushed granite used for the bulk of the project, meeting the requirements of BS 8500-1, supplied in both 10mm and 20mm fractions. Natural gravel was supplied in bulk in 4/10 and 10/20 sizes. A commercially available synthetic fly ash based lightweight aggregate was used during the project, supplied in sealed 25kg containers supplied by CEMEX Lytag.

Both the chemical and physical characteristics can be found in Table 3.2 and Table 3.3 respectively, with the particle size distribution shown in Figure 3.4. All the coarse aggregates were washed and dried in the laboratory, apart from lightweight aggregate. Once washed, the lightweight aggregate was placed back into the container where it was saturated due to having a high-water absorption.

3.3.6 Fine Aggregate

A source of natural local sand was used for the major of the project, though a synthetic lightweight sand was also used in the project. Similar to lightweight aggregate, the sand is produced from fly ash though due to the nature of the sand, bulk of sand made up by dust, the sand was not saturated in water. The chemical and physical characteristics are shown in Table 3.2 and Table 3.3. The particle size distribution is plotted in Figure 3.4.

3.3.7 Mix Water

For concrete and mortar production, mains water was used, however, some of the testing procedures required distilled/deionised water to prevent impurities affecting test results.

Table 3.1 Chemical and physical characteristics of cementitious materials

Property	CEM I	Fly Ashes					GGBS	LS
		DFA 1	DFA 2	DFA 3	DFA 4	DFA 5		
Chemical Composition[1], %								
SiO_2	18.6	43.4	48.0	46.7	47.6	49.7	32.3	1.6
Al_2O_3	4.0	18.6	21.5	27.0	22.4	23.8	9.8	1.0
Fe_2O_3	3.2	8.7	7.3	6.0	9.2	7.9	0.6	0.2
CaO	63.1	4.4	4.5	2.1	5.6	2.3	38.6	75.0
MgO	2.3	-	1.9	1.1	1.6	1.7	8.0	0.3
SO_3	3.9	2.3	2.0	0.6	2.0	1.4	1.9	0.1
K_2O	0.7	2.6	2.4	2.7	2.0	2.9	0.4	-
Na_2O	0.3	-	1.4	0.7	0.7	0.9	0.3	-
TiO_2	0.3	1.1	1.0	1.0	0.9	0.9	0.6	-
P_2O_5	-	0.4	0.6	0.8	0.6	0.2	-	-
MnO	-	-	-	-	-	-	0.3	-
L.O.I.	4.6	5.1	4.1	4.6	5.3	5.2	0.5	20.8
Compound Composition, %								
C_3S	67.4	-	-	-	-	-	-	-
C_2S	7.4	-	-	-	-	-	-	-
C_3A	5.1	-	-	-	-	-	-	-
C_4AF	9.8	-	-	-	-	-	-	-
Compressive Strength[2] EN 196-1, MPa								

3 days	42.5	32.1	30.7	21.6	20.4	21.9	19.7	-
7 days	45.3	33.3	35.0	29.5	32.3	32.5	33.9	-
28 days	49.9	34.0	37.8	40.4	33.1	38.3	50.8	-
Particle Size, μm								
D_{10}	3.1	3.5	1.7	2.6	3.0	2.7	1.8	1.4
D_{50}	15.9	16.1	10.7	17.7	24.5	24.5	11.0	5.9
D_{90}	44.5	67.5	64.5	81.8	110.0	126.2	32.7	19.6
Fineness %	-	10.5	8.1	18.7	21.2	25.3	-	-
Specific Gravity	3.15			2.25 – 2.30			2.91	-

(1)Calculated by author using XRF. (There are some discrepancies in the data due to calibration issues with the XRF.

(2)Compressive strength undertaken by author.

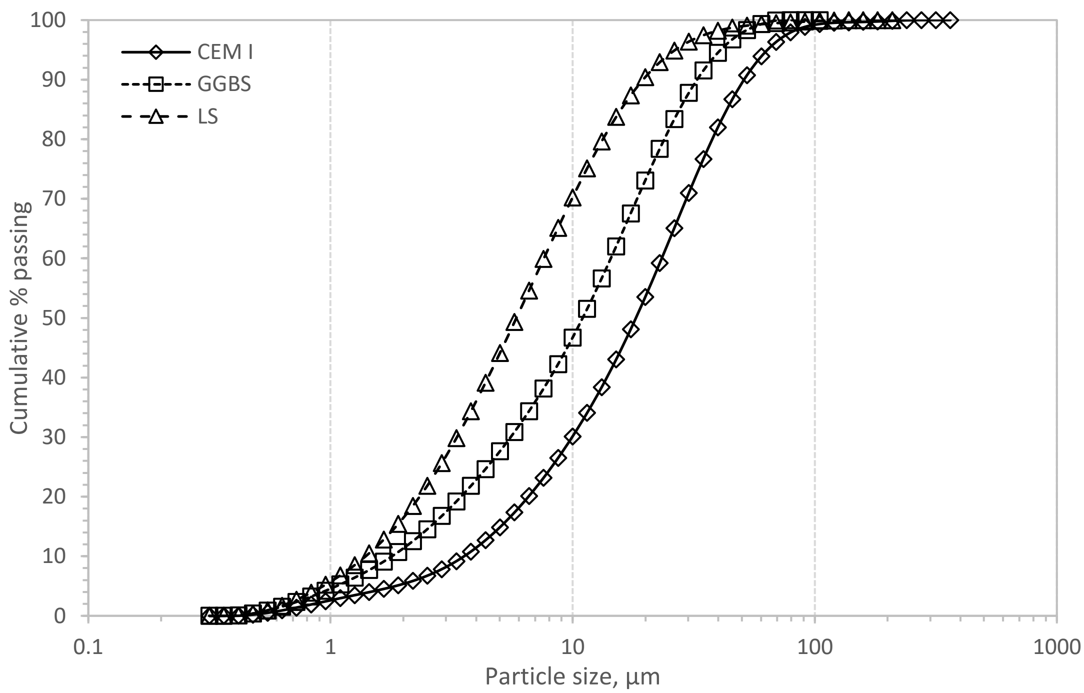


Figure 3.2 Particle size distribution for CEM I, GGBS and Limestone

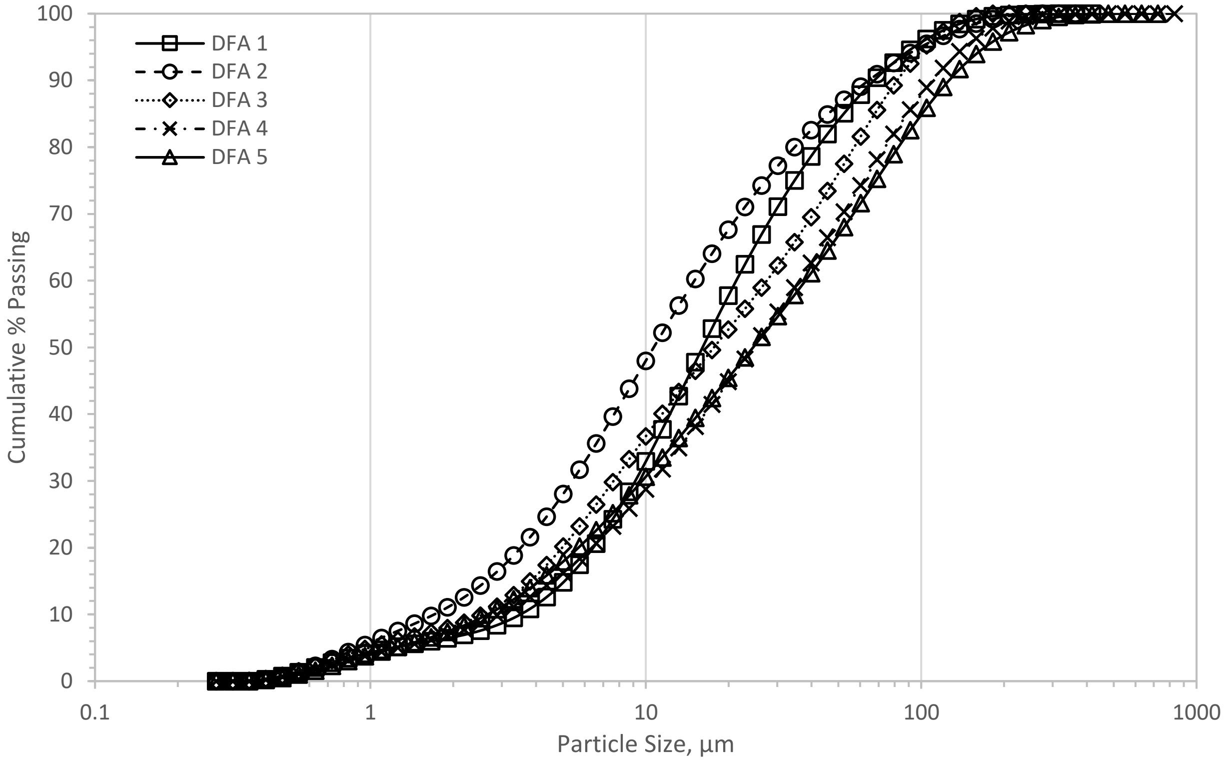


Figure 3.3 Particle size distribution for various fly ashes

3.3.8 Water Reducing Admixture

Two water reducing admixtures were used in the concrete production in accordance with BS EN 934 Part 2:2009 to reach a target slump of class S3 (100-150mm) as described in BS EN 206. The admixture properties are shown in Table 3.4.

3.3.9 Air Entraining Admixture

Two air entraining admixtures were used during the project conforming with BS EN 934-2 to achieve a target air content of 4.5% in accordance with BS 8500-1. The properties of the admixtures are shown in Table 3.4.

Table 3.2 Chemical characteristics of 0/4, 4/10 and 10/20 aggregates

Oxide	Bulk Oxide Content, %						
	Fine Aggregate (0/4 mm)		Coarse Aggregate (4/20 mm)				
	Natural Sand	Lightweight Sand	Granite		Natural Gravel		Lightweight
			4/10	10/20	4/10	10/20	4/14
CaO	3.2	2.8	1.6	1.4	2.2	1.5	2.4
SiO_2	64.3	48.2	68.8	75.2	66.2	59.7	53.3
Al_2O_3	12.2	22.0	14.6	13.5	13.5	14.3	22.8
Fe_2O_3	4.1	9.3	2.3	2.1	4.6	4.1	8.5
MgO	3.4	-	0.8	0.6	3.1	3.4	1.9
K_2O	2.4	2.9	3.9	3.3	2.3	2.4	2.9
Na_2O	2.2	1.0	3.3	3.0	3.2	3.3	1.0
TiO_2	0.7	1.0	0.3	0.3	0.8	0.8	1.0
P_2O_5	0.2	0.2	0.2	0.2	0.2	0.2	0.3
L.O.I.	3.9	2.5	1.4	1.9	2.7	2.7	1.9

- denotes no trace

Table 3.3 Physical characteristics of 0/4 mm, 4/10 mm and 10/20 mm aggregates

Material	Flakiness Index, % (BS EN 933-3)	Water Absorption, % (BS EN 1097-6)	Los Angeles Coefficient (BS EN 1097-2)	Freeze-Thaw Resistance (BS EN 1367-1)	Magnesium Sulphate Soundness Value (BS EN 1367-2)	Relative Density BS EN 1097-6)	Loose bulk Density, kg/m^3 (BS EN 1097-3)
Natural Sand	-	2.6	-	-	-	2.64	1610
Lightweight Sand	-	14.9	-	-	-	-	1000
Crushed Granite							
4/10 mm	14	0.8	-	1	1	2.63	1250
10/20 mm	14	0.5	22	1	2	2.63	1285
Natural Gravel							
4/10 mm	10	1.6	-	3	5	2.54	1495
10/20 mm	12	2.2	26	3	6	2.54	1460
Lightweight Aggregate							
4/14 mm	-	14.0	28[1)]	3	38[2)]	1.87	790

[1)]BS EN 1097-2 does not describe the LA test for lightweight aggregate, however, the standard was used to accommodate it

[2)]BS EN 1367-2 does not describe the magnesium sulphate test for lightweight aggregate, however, the standard was used to accommodate it

- denotes no data

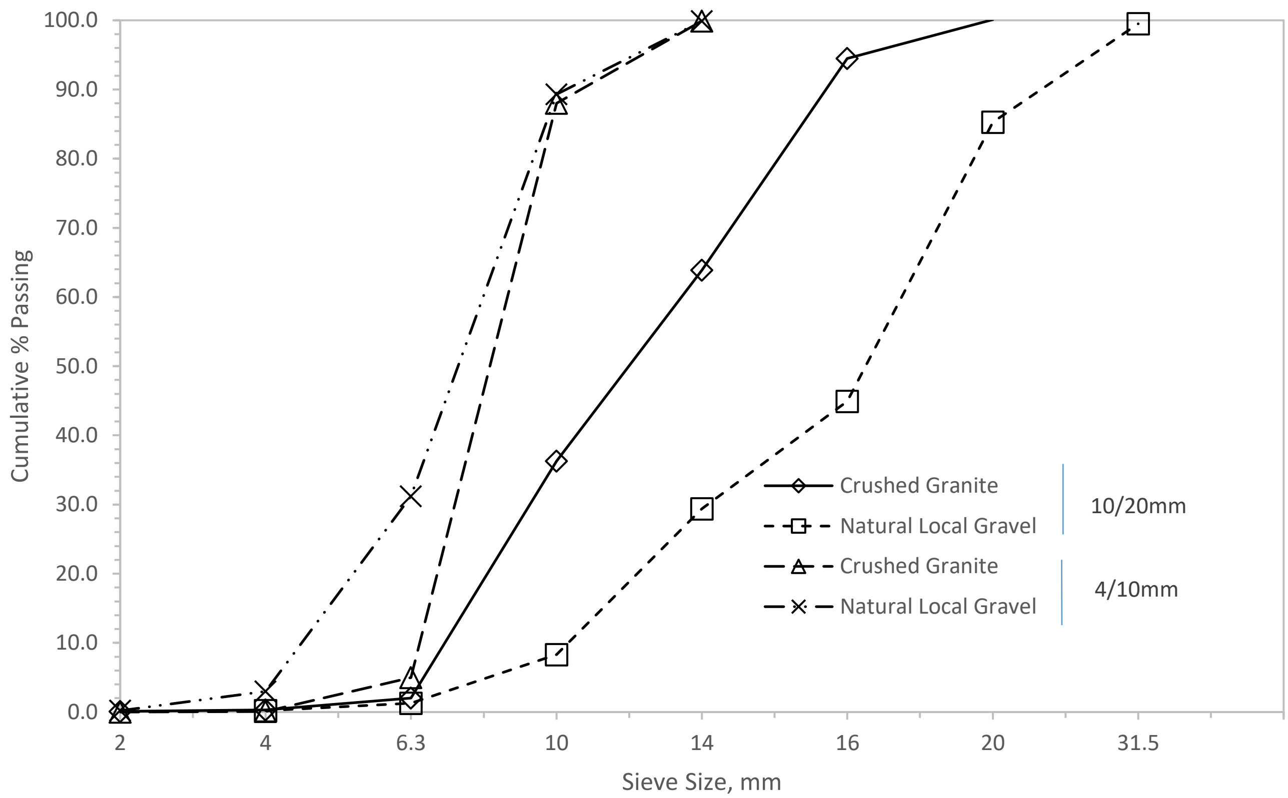


Figure 3.4 Particle size distribution of 4/10mm and 10/20mm coarse aggregates used on the project

Table 3.4 Chemical and physical properties of admixtures according to the manufactures

Characteristics	**Admixture Type**					
	Water Reducer/Superplasticizer		Air Entrainer		Viscosity Modifier	Accelerator
	SP 1	SP 2	AE 1	AE 2		
Manufacturer / Product	BASF Glenium Sky 569	Fosroc Auracast 200	BASF MasterAir 130	Sika AER 46	BASF Master Matrix SDC 150	BASF Master X-Seed 100
Description						
Type	Water reducing admixture based on polycarboxylate ether adhering to BS EN 934-2	Water reducing admixture adhering to BS EN 934-2	Liquid air entraining admixture adhering to BS EN 934-2	Air entraining admixture with alcohols, C10-16, ethoxylated, sulphates, sodium salts adhering to BS EN 934-2	Viscosity modifying admixture with modified surfactants adhering to BS EN 934-2	Accelerating admixtures with inorganic salts and modified organic compounds adhering BS EN 934-2
Appearance/colours	Light brown	Dark strawberry	Yellow	Clear	Clear	White
Form	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Odour	Characteristic	Slight	Soap-like	Soap-like	Odourless	Odourless
Chemical Properties						
pH Value	6.0 ± 1.0	7.0 ± 1.0	10 ± 1.0	6.0 ± 1.0	6.5 ± 1.0	11.0 ± 1.0
Chloride Content	≤ 0.1% by mass	< 0.1% by mass	nd	< 0.1% by mass	< 0.1% by mass	< 0.1% by mass
Alkali Content	≤ 2.0% by mass	< 0.5% by mass	nd	< 0.1% by mass	< 0.1% by mass	< 4.0% by mass
Physical Properties						
Freezing Point	nd	Sensitive to freezing	nd	1°C	1°C	nd
Boiling Point	≈ 100°C	≈ 100 °C	> 100°C	nd	> 100°C	> 100°C
Vapour Pressure	2.3 kPa at 20°C	nd	nd	nd	2.3 kPa at 20°C	2.3 kPa at 20°C
Specific Gravity	1.08 @ 20°C	1.1 @ 20°C	1.01 @ 20°C	1.0 @ 20°C	1.01 @ 20°C	1.135 @ 20°C
Air Entrainment	nd	< 2% additional air is entrained	≥ 2.5% by volume of reference mix and total air content between 4 – 6%	nd	≤ Reference mix + 2.0%	nd

nd – no data

3.4 Concrete Mix Proportions - Phase 1a Laboratory Study

Four cementitious materials were used in the project. Each material had a series of concretes cast varying different parameters:

- Series 1 varied the target strength (20-60 MPa) with no air entrainment;
- Series 2 varied the target strength (20-50 MPa) with a target air content of 4.5% ± 0.5%;
- Series 3 fixed the target strength to 40 MPa but varied target air content of 7%, 9.5% and 12% and;
- Series 4 fixed the target strength to 40 MPa but varied the addition content.

It should be noted that for CEM I there was no Series 4 due to the inability to vary the cement content that had no replacement. Using air entrainment, there is a need to increase the design strength to cope with the strength whilst entraining air . For Series 2 the design strength was only able to reach 50 MPa rather than 60 MPa. The design of the concrete was done using the guidance document, Building Research Establishment (BRE) design guide (Teychenne et al., 1997), ensuring that a constant workability was achieved conforming to BS EN 206-1 slump class S3 (100 to 150mm) and an air content of 4.5% ± 0.5%. The tables also show there are many of the concretes that do not comply with BS 8500 regarding meeting the requirements for either XF3 or XF4 exposure class. According to the standards there are requirements outlined in BS 8500 Table A.9 whether a concrete complies with a particular class.

For XF3 and XF4, Table 3.5 details the minimum requirements for these classes. Each table details which of the concretes are in accordance with BS 8500. These concretes will be used for Phase 1a of the study reviewing laboratory produced concretes for freeze-thaw. Details of the bulk reference concrete mixes are shown in Table 3.6 to Table 3.9 with their respective fresh properties including the slump and air contents and compressive strengths at 3, 7 and 28 days curing.

Table 3.5 Minimum requirements for concretes for XF3 and XF4 exposure classes

Requirement	**XF3**		**XF4**	
	With air entrainment	No air entrainment	With air entrainment	No air entrainment
Minimum Strength Class	C25/30	C40/50 or LC40/44	C28/35	C40/50 or LC40/44
Maximum w/c Ratio	0.60	0.45	0.55	0.45
Minimum cement content of a maximum aggregate size of 20 mm and 4.5% air content (kg/m^3)	280	340	300	340

Table 3.6 Mix proportions CEM I concretes and their fresh properties and standard cured compressive strength results

Mix Code	Design Strength, MPa	Constituent Materials, kg/m³					w/c Ratio	Admixture Contents, %1)		Target Air Content, %	Conforming to BS 8500		Fresh Properties		Compressive Strength, MPa			
		Cement/ Addition	Water	Aggregates														
		CEM I		0/4	4/10	10/20		SP	AE		XF3	XF4	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %2)
Series 1 Non-Air Entrained																		
M1	20	255	190	780	375	750	0.75	0.67	-	-	N a,b,c)	N a,b,c)	150	1.2	20.2	22.3	29.0	3.29
M2	30	298	189	755	373	745	0.63	0.57	-	-	N a,c)	N a,b,c)	140	1.2	26.5	29.5	38.4	0.40
M3	40	349	187	728	369	738	0.54	0.48	-	-	N b,c)	N b,c)	130	1.6	35.4	39.0	49.7	1.43
M4	50	404	185	701	365	730	0.46	0.41	-	-	N c)	N c)	100	1.8	42.4	51.5	59.5	2.35
M5	60	457	183	674	361	722	0.4	0.42	-	-	Y	Y	110	1.7	53.1	60.5	69.9	2.68
Series 2 Air Entrained																		
M6	20	298	188	759	372	744	0.63	0.57	0.67	4.5	N a,b,c)	N a,b,c)	140	4.5	22.0	23.8	30.5	1.80
M7	30	358	186	726	368	736	0.52	0.47	0.55	4.5	Y	N b)	140	4.3	29.7	31.1	39.5	1.77
M8	40	409	185	696	365	730	0.45	0.41	0.48	4.5	Y	Y	110	4.2	32.6	37.6	47.8	1.60
M9	50	463	183	666	362	723	0.4	0.38	0.42	4.5	Y	Y	90	4.7	35.0	45.1	52.9	5.54
Series 3 Varied Air Content																		
M10	40	409	185	696	365	730	0.45	0.41	0.74	7.0	Y	Y	110	6.8	25.8	35.7	41.8	3.48
M11	40	409	185	696	365	730	0.45	0.41	1.00	9.5	Y	Y	140	9.0	27.6	32.2	38.6	3.24
M12	40	409	185	696	365	730	0.45	0.41	1.26	12.0	Y	Y	110	11.0	27.3	32.0	40.4	1.03

(1)% weight of total cement content

(a)Failed specification in minimum cement content

(b)Failed specification in minimum strength

(c)Failed specification in maximum w/c ratio

(2)Coefficient of Variation for the compressive strengths at 28 days only

Table 3.7 Mix proportions CEM II/B-V concretes and their fresh properties and standard cured compressive strength results

Mix Code	Design Strength, MPa	Constituent Materials, kg/m³: Cement/Additions			Aggregates			w/c Ratio	Admixture Contents, % [1)]		Target Air Content, %	Conforming to BS 8500		Fresh Properties		Compressive Strength, MPa			
		CEM I	PFA	Water	0/4	4/10	10/20		SP	AE		XF3	XF4	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %
Series 1 Non-Air Entrained																			
M13	20	169	91	170	794	382	763	0.69	0.68	-	-	N [a,b,c)]	N [a,b,c)]	170	1.0	12.2	14.7	22.7	2.86
M14	30	197	106	169	767	379	757	0.58	0.68	-	-	N [a,b,c)]	N [a,b,c)]	120	1.3	17.7	20.0	27.4	0.97
M15	40	231	124	167	739	374	749	0.49	0.68	-	-	N [b,c)]	N [b,c)]	120	1.5	23.7	27.6	39.4	1.83
M16	50	266	143	165	710	370	739	0.42	0.63	-	-	Y	Y	110	1.6	32.1	36.0	49.7	4.01
M17	60	301	162	163	681	365	730	0.37	0.64	-	-	Y	Y	100	1.8	37.7	48.1	60.0	0.82
Series 2 Air Entrained																			
M18	20	196	106	169	771	378	756	0.66	0.58	0.8	4.5	N [a,b,c)]	N [a,b,c)]	130	4.4	11.3	13.4	21.8	4.12
M19	30	236	127	167	736	373	746	0.55	0.66	0.66	4.5	Y	N [b)]	130	4.3	16.5	20.1	29.8	3.01
M20	40	269	145	165	705	370	739	0.45	0.62	0.57	4.5	Y	Y	100	4.7	24.2	29.2	36.4	4.39
M21	50	304	164	163	673	366	732	0.39	0.59	0.5	4.5	Y	Y	120	4.5	31.6	38.3	46.2	1.42
Series 3 Varied Air Content																			
M22	40	269	145	165	705	370	739	0.39	-	-	7.0	Y	Y	120	7.3	21.1	24.9	37.2	1.34
M23	40	269	145	165	705	370	739	0.38	-	-	9.5	Y	Y	100	8.8	22.1	24.3	35.4	0.75
M24	40	269	145	165	705	370	739	0.36	-	-	12.0	Y	Y	100	10.5	19.9	22.2	31.9	0.48
Series 4 Varied PFA Content (45%, 55%, 65%)																			
M25	40	212	173	162	716	375	751	0.4	-	-	4.5	Y	Y	170	4.7	15.3	21.6	31.6	1.45
M26	40	173	212	158	717	376	752	0.4	-	-	4.5	Y	Y	120	4.5	10.2	14.9	23.6	1.53
M27	40	136	251	153	719	377	754	0.4	-	-	4.5	Y	Y	100	4.5	7.7	10.2	19.4	2.93

[(1)] % weight of total cement content
[(a)] Failed specification in minimum cement content
[(b)] Failed specification in minimum strength
[(c)] Failed specification in maximum w/c ratio

[(2)] Coefficient of Variation for the compressive strengths at 28 days only

Table 3.8 Mix proportions CEM III/A concretes and their fresh properties and standard cured compressive strength results

Mix Code	Design Strength, MPa	Constituent Materials, kg/m³						w/c Ratio	Admixture Contents, % [1)]		Target Air Content, %	Conforming to BS 8500		Fresh Properties		Compressive Strength, MPa			
		Cement/ Additions		Water	Aggregates														
		CEM I	GGBS		0/4	4/10	10/20		SP	AE		XF3	XF4	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, % [2)]
Series 1 Non-Air Entrained																			
M28	20	115	140	185	781	376	751	0.73	0.67	-	-	N [a,b,c)]	N [a,b,c)]	160	1.0	10.9	16.5	25.5	2.16
M29	30	134	164	184	756	373	746	0.62	0.57	-	-	N [a,b,c)]	N [a,b,c)]	150	1.0	14.9	22.0	32.8	1.10
M30	40	157	192	182	728	369	738	0.52	0.48	-	-	N [b,c)]	N [b,c)]	140	1.4	20.1	29.9	41.1	2.97
M31	50	182	222	180	700	365	729	0.45	0.41	-	-	Y	Y	120	1.4	24.3	36.8	51.6	2.91
M32	60	206	251	178	673	360	721	0.39	0.36	-	-	Y	Y	100	1.4	28.6	44.0	60.8	2.21
Series 2 Air Entrained																			
M33	20	134	164	184	759	372	744	0.62	0.57	0.67	4.5	N [a,b,c)]	N [a,b,c)]	150	4.5	11.8	18.1	25.5	1.80
M34	30	161	197	181	726	368	736	0.51	0.47	0.55	4.5	Y	N [b)]	130	4.6	16.4	23.4	33.8	1.78
M35	40	184	225	180	695	365	729	0.44	0.4	0.48	4.5	Y	Y	120	4.7	19.1	28.6	42.2	1.09
M36	50	208	254	178	664	361	722	0.39	0.35	0.42	4.5	Y	Y	100	4.0	24.5	36.2	51.0	0.79
Series 3 Varied Air Content																			
M37	40	184	225	180	695	365	729	0.44	0.41	0.74	7.0	Y	Y	110	6.5	24.9	29.2	38.8	4.11
M38	40	184	225	180	695	365	729	0.44	0.41	1.00	9.5	Y	Y	120	8.5	23.9	27.8	37.5	0.62
M39	40	184	225	180	695	365	729	0.44	0.41	1.35	12.0	Y	Y	120	8.6	20.5	27.9	37.4	2.30
Series 4 Varied GGBS Content (65%, 75%, 85%)																			
M40	40	184	225	180	695	365	729	0.44	0.41	0.48	4.5	Y	Y	120	4.4	21.3	24.8	36.8	2.32
M41	40	150	258	180	695	364	729	0.44	0.41	0.48	4.5	Y	Y	130	4.4	19.6	25.4	36.2	3.98
M42	40	115	293	180	694	364	728	0.44	0.41	0.48	4.5	Y	Y	130	4.2	17.2	23.4	34.2	5.42

(1)% weight of total cement content

(a)Failed specification in minimum cement content

(b)Failed specification in minimum strength

(c)Failed specification in maximum w/c ratio

(2)Coefficient of Variation for the compressive strengths at 28 days only

Table 3.9 Mix proportions CEM II/A-L concretes and their fresh properties and standard cured compressive strength results

Mix Code	Design Strength, MPa	Constituent Materials, kg/m^3						w/c Ratio	Admixture Contents, %[1]		Target Air Content, %	Conforming to BS 8500		Fresh Properties		Compressive Strength, MPa			
		Cement/ Additions		Water	Aggregates														
		CEM I	LS		0/4	4/10	10/20		SP	AE		XF3	XF4	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %[2]
Series 1 Non-Air Entrained																			
M43	20	204	51	190	778	374	748	0.75	0.59	-	-	N [a,b,c]	N [a,b,c]	160	1.0	11.4	14.6	19.8	1.55
M44	30	238	59	188	753	371	743	0.63	0.5	-	-	N [a,b,c]	N [a,b,c]	160	1.3	13.9	20.8	26.3	2.44
M45	40	279	69	186	726	368	735	0.54	0.42	-	-	N [a,c]	N [a,c]	140	1.3	20.7	28.3	36.2	0.55
M46	50	325	78	184	698	363	727	0.46	0.36	-	-	N [c]	N [c]	140	1.5	31.7	36.9	48.1	2.11
M47	60	369	86	182	671	359	719	0.40	0.32	-	-	Y	Y	110	1.6	42.7	51.5	59.9	3.73
Series 2 Air Entrained																			
M48	20	237	59	188	756	371	742	0.63	0.5	0.6	4.5	N [a,b,c]	N [a,b,c]	150	4.4	14.8	18.6	23.6	2.20
M49	30	285	71	186	723	367	733	0.52	0.41	0.49	4.5	Y	N [b]	130	4.3	20.4	25.2	30.7	1.67
M50	40	326	81	184	693	364	727	0.45	0.36	0.43	4.5	Y	Y	100	4.4	25.6	32.1	39.7	1.15
M51	50	369	92	182	662	360	720	0.4	0.37	0.37	4.5	Y	Y	100	4.5	32.2	39.1	48.0	2.87
Series 3 Varied Air Content																			
M52	40	326	81	184	693	364	727	0.45	0.36	0.67	7.0	Y	Y	130	6.8	24.0	26.1	32.6	3.02
M53	40	326	81	184	693	364	727	0.45	0.36	0.91	9.5	Y	Y	130	6.6	27.1	28.8	36.8	0.63
M54	40	326	81	184	693	364	727	0.45	0.36	1.14	12.0	Y	Y	130	7.4	25.6	27.8	33.4	3.98
Series 4 Varied LS Content (30%, 40%, 50%)																			
M55	40	263	113	186	700	367	734	0.45	0.36	0.43	4.5	Y	Y	130	4.5	21.0	23.1	28.0	1.83
M56	40	226	150	186	698	366	732	0.45	0.36	0.43	4.5	Y	Y	130	4.4	14.6	17.8	22.3	2.26
M57	40	187	188	185	697	365	731	0.45	0.36	0.43	4.5	Y	Y	130	4.3	10.9	12.9	16.6	1.20

(1)% weight of total cement content

(2)Coefficient of Variation for the compressive strengths at 28 days only

(a)Failed specification in minimum cement content

(b)Failed specification in minimum strength

(c)Failed specification in maximum w/c ratio

Throughout the project various mixes were cast to look at various aspects on the freeze-thaw test method and how changing different parameters would affect the durability of the concrete. In order to track the various aspects being investigated during the project different mix codes were used to identify which was which. Table 3.10 details what the mix code describes, and the number of mixes cast in the study.

Table 3.10 Abbreviations used to describe the various mixes cast on the project

Abbreviation	**Number of Mixes**	**Abbreviation Description**
M	57	Bulk mixing testing strength, air content & replacement content
GV	8	Mixes containing gravel aggregate
IC	5	Concretes produced by industry
CS	8	Mixes done to test cast surface durability
AC	12	Admixture compatibility mixes
DFA	10	Concrete containing different types of fly ash
SC	8	Freeze-thaw testing with various salt concentration
LWA	9	Concrete with lightweight aggregate
CFT	8	Concretes tested in carbonation then freeze-thaw
V1 & V2	8 each	Concretes subjected to different temperature profiles

Concretes containing gravel aggregate were cast for comparison to the bulk reference concretes to determine how the freeze-thaw durability is influenced by a different aggregate type. In terms of the mix design and portioning, these have not changed only the type of aggregate used. As the gravel aggregate is more porous than granite it will provide a good comparison to determine the effects of different aggregate classifications for Phase 1a. These mix designs are shown in Table 3.11.

In order to correlate the data from Phase 1a, a series of concretes were produced by industrial concrete producers to compare those produced in the laboratory and those used throughout the construction industry in line with the standards. The parameters outlined are the same as those for laboratory concretes with a slump class S3 and a minimum air content of 4.5%. Table 3.12 shows the mix proportions for the concretes along with the compressive strength at 3, 7 and 28 days, slump and air content of the fresh concrete. This will be covered in Phase 3 of the study.

Table 3.11 Mix designs for concretes cast using gravel as aggregate

Mix Code	Constituent Materials, kg/m³								w/c Ratio	Admixture Contents, %[1)]		Target Air Content, %	Fresh Properties		Compressive Strength, MPa			
	Cement/Addition				Water	Aggregates												
	CEM I	PFA	GGBS	LS		0/4	4/10	10/20		SP	AE		Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %[2)]
GV1	283	-	-	-	151	590	299	598	0.54	1.09	-	-	130	1.3	26.9	33.3	42.8	4.60
GV2	332	-	-	-	150	565	296	592	0.45	1.09	2.0	4.5	130	4.5	26.5	33.7	39.9	3.54
GV3	186	100	-	-	135	597	302	605	0.47	1.3	-	-	110	1.4	17.8	22.1	31.6	2.25
GV4	218	117	-	-	134	571	299	599	0.4	1.96	2.4	4.5	120	4.4	17.0	23.2	32.7	4.17
GV5	127	-	156	-	147	590	299	598	0.52	1.09	-	-	110	1.5	18.6	23.9	34.9	3.63
GV6	149	-	182	-	146	564	296	592	0.44	1.09	1.0	4.5	100	4.5	20.1	27.0	37.9	2.79
GV7	226	-	-	56	151	588	298	596	0.54	1.09	-	-	130	1.5	23.2	28.3	37.4	2.02
GV8	265	-	-	66	150	563	295	590	0.45	1.09	2.0	4.5	120	4.7	23.2	27.9	35.3	3.03

[(1)] % weight of total cement content   [(2)] Coefficient of Variation for the compressive strengths at 28 days only

Table 3.12 Mix designs for industry produced concretes

Mix Code	Cement Type	Cement/ Addition, kg/m³	Water, kg/m³	w/c ratio	Aggregate, kg/m³		Admixture, % wt of cement		Fresh Properties		Compressive Strength, MPa			
					0/4	4/20	SP	AEA	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %
IC-M02	CEM I	335	184	0.55	790	1057	0.6	0.15	120	4.7	25.7	30.9	41.0	1.20
IC-M03	CEM III/A	410	172	0.42	608	1102	0.7	0.19	100	5.8	30.3	44.9	58.5	1.43
IC-M04	CEM I	385	172	0.45	600	1080	0.37	0.08	110	6.3	34.2	37.6	43.9	2.88
IC-M05	CEM II/B-V	385	146	0.38	686	1010	0.6	0.1	130	4.6	37.9	46.7	58.3	6.45

[(1)] % weight of total cement content   [(2)] Coefficient of Variation for the compressive strengths at 28 days only

3.5 Test Methods and Instrumentation

Throughout this project, a series of various tests have been used to determine many properties, fresh and hardened, durability properties of both concrete and its aggregates and characterisation of the materials used. Table 3.13 outlines the main standards which the project has complied to along with the standard precision statement.

3.5.1 Mixing of Concrete

Mixing of the concrete was conducted using a pan mixer with a maximum capacity of 0.035m^3. Mixing was carried out in accordance with BS 1881-125:2013. A damp cloth is used first to dampen the pan and mixing paddles to reduce water adsorption by the metal. The aggregate is added and dry mixed for 30 seconds before half of the water is added and mixed for a further 30 seconds. After 8 minutes of water absorption, the cement (and any additional binder) is added to the mixer and mixed for 1 minute. The remaining water is then added along with admixtures and then mixed for a further 2 minutes. Once mixed the concrete was hand mixed to ensure that all materials had been thoroughly mixed.

All aggregates were dry before mixed into the concrete and the additional water (which considered the water absorption) added during the mixing process. An additional preparation step was completed for the lightweight aggregate due to the high-water absorption value of 14%. It was pre-soaked before being added to the mixer otherwise it which would affect the available free water in the mix. The aggregate was left in a bucket of water for 24 hours before being removed and surfaced dried then afterwards it was mixed in the concrete as per above. Had the additional water for the lightweight aggregate been added during the mixing process, it would affect the concrete properties as there would not be enough time for the aggregate to absorb the full amount of additional water.

3.5.2 Slump Test

The slump test determines the workability of a concrete by measuring how much the concrete ‘slumps’ once the mould is removed. The test is carried out in accordance with BS EN 12350-2:2009 by filling a 300mm high cone mould in three equal layers and tamping the concrete 25 times with a steel rod. Tamping is carried out after each layer is added to the cone and once filled and tampered the excess is removed from the top and levelled using a trowel. Then once immediately levelled, the cone is gently removed from the concrete to stop excessive slumping of the concrete. Afterwards, the cone is placed next to the concrete and a steel rule is used to measure the difference in height between the mould and the highest point of the sample. This value is rounded to the nearest 10mm.

Table 3.13 List of standards used during the project detailing the name, standard no. and the materials used

Name of Standard	Standard Identification No.	Materials Tested	Standard Precision Statement	
			r	R
Testing Fresh Concrete				
Methods for mixing and sampling fresh concrete in the laboratory	BS 1881-125:2013	CEM I, CII-B, CIII, CII-L	nd	nd
Slump Test	BS EN 12350-2:2009	CEM I, CII-B, CIII, CII-L	16%	25%
Air Content Pressure Methods	BS EN 12350-7:2009	CEM I, CII-B, CIII, CII-L	0.4%	1.3%
Testing Hardened Concrete				
Compressive Strength of Specimens	BS EN 12390-3:2009	CEM I, CII-B, CIII, CII-L	9%	15.1%
Determination of the Potential Carbonation Resistance of Concrete. Accelerated Carbonation Method	BS 1881-210:2012	CEM I, CII-B, CIII, CII-L	nd	nd
Freeze-Thaw Resistance - Scaling	CEN/TS 12390-9:2016	CEM I, CII-B, CIII, CII-L	17%	31%
Chemical and Physical Properties of Aggregates				
Determination of Resistance to Freezing and Thawing	BS EN 1387-1:2007	Granite, Gravel, Lightweight	nd	nd
Magnesium Sulphate Test	BS EN 1387-2:2009	Granite, Gravel, Lightweight	4.2%	5.5%
Methods for the Determination of Resistance to Fragmentation	BS EN 1097-2:2010	Granite, Gravel, Lightweight	1.3%	3.7%
Determination of Loose Bulk Density and Voids	BS EN 1097-3:1998	Granite, Gravel, Lightweight	nd	nd
Determination of Particle Density and Water Absorption	BS EN 1097-6:2013	Granite, Gravel, Lightweight	0.3%	0.4%
Air Void Analysis				
Determination of Air Void Characteristics in Hardened Concrete	BS EN 480-11:2005	CI, CII-B, CIII, CII-L	nd	nd
Microscopical Determination of Parameters of the Air Void System in Hardened Concrete	ASTM C 457:2009	CI, CII-B, CIII, CII-L	nd	nd

nd - no data

r – Repeatability

R - Reproducibility

3.5.3 Air Content Test of Fresh Concrete

The air content of concrete was measured on all the concretes that were cast for the duration of this project. The method chosen was the pressure gauge method in accordance with BS EN 12390-7:2009 as this test method is the more popular choice and can be conducted in various conditions.

The test is conducted by filling the container with three equal layers of concrete then compacting once each layer has been added. Each layer of the concrete is vibrated for approximately 10 seconds (this varies depending on the workability) to remove entrapped air as this will affect the air content result. When all three layers have been compacted, a float is used to remove any excess concrete on the top to create a level surface before the top section is added.

The flanges of the apparatus are cleaned removing any excess concrete possibly causing an uneven seal around the container when clamped down. Once a tight seal is created, the valves are opened, and water is poured into the container whilst tapped lightly to expel any remaining entrapped air. The valves are closed once water emerges from the other valve and the main bleeder valve is closed. The air is pumped into the air chamber until the gauge needle is on the initial pressure line (0%). The gauge is given a few seconds to stabilize (due to the temperature of the compressed air cooling), the air is pumped into the container, compressing the concrete. The air escapes the main air chamber and the pressure gauge records the pressure used on the concrete.

3.5.4 Compressive Strength Test

Compressive strength tests were carried out using a Matest compression machine complying with 12390-3:2009. Three 100mm cubes were tested at a load rate of 7 kN/s at their respective test age and an average of the three was taken. The results were recorded to the nearest 0.1 MPa.

3.5.5 Methods for Testing Aggregates for Freeze-Thaw Durability

3.5.5.1 Freeze-Thaw Testing of Aggregates Using Freeze-Thaw Chamber

Freeze-thaw durability of aggregates is conducted in accordance with BS EN 1367-1:2007. Two test specimens are weighed out depending on the aperture size, for this test method two aperture sizes were used, to test both 5/10 and 10/20 aggregates. The specimens are placed into metal cans with water and are left to soak for 24 hours, ensuring that a minimum cover of 10 mm is provided. After 24 hours the specimens are placed into the freeze-thaw chamber following the temperature cycle shown in Figure 3.5.

The specimens would be subject to 10 cycles with one cycle (with a duration of 24 hours) carried out as follows:

I. Temperature of the chamber is reduced from 20°C ± 5°C to (0 -1)°C in (150 ± 60) minutes and held at (0 -1)°C for (210 ± 90) minutes;

II. The, the temperature is reduced from (0 -1)°C to -17.5°C ± 2.5°C in (180 ± 60) minutes and held at this temperature for a further 240 minutes;

III. After each freezing cycle, the cans are then removed from the chamber and placed into a water bath with a temperature measuring 20°C. Thawing is complete when the temperature inside the cans is 20°C;

IV. Once the thawing cycle is complete the cans remain in the water bath for the remainder of the freeze-thaw cycle.

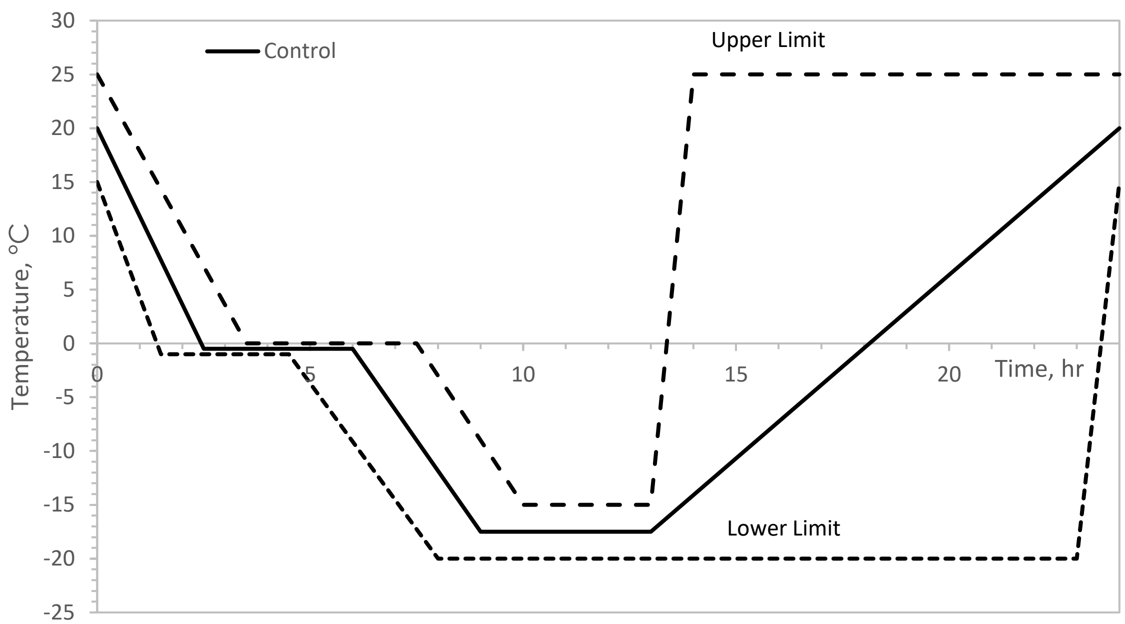


Figure 3.5 Temperature profile for freeze-thaw durability testing of aggregates

The material from the cans is drained and sieved using a test sieve which is half of the lower size (for example, if 8mm to 16mm fraction size is tested then a 4mm sieve would be used) then placed in an oven 110°C ± 5°C until a constant mass before allowing to cool to ambient temperature. The mass loss (F) is calculated as a percentage of the total mass:

$$F = \frac{M_1 - M_2}{M_1} \times 100 \qquad (5)$$

where M_1 = initial dry total mass in grams

M_2 = finial dry total mass in grams

3.5.5.2 Magnesium Sulphate Test

Complying with BS EN 1367-2: 2009, the magnesium sulphate test is another method for determining an aggregate's freeze-thaw performance. 1500g of Magnesium sulphate heptahydrate reagent is dissolved into 1 litre of deionised/distilled water at a temperature of 40°C ensuring full saturation is achieved. For the test to be carried out a minimum of 3 litres is required. Once full saturation is achieved the solution is left for 48 hours at a temperature of 20°C. Two test specimens are weighed out with a mass of 425g ± 0.1g, that have passed a 14mm sieve is retained on a 10mm sieve, are place into mesh baskets, shown in Figure 3.6.

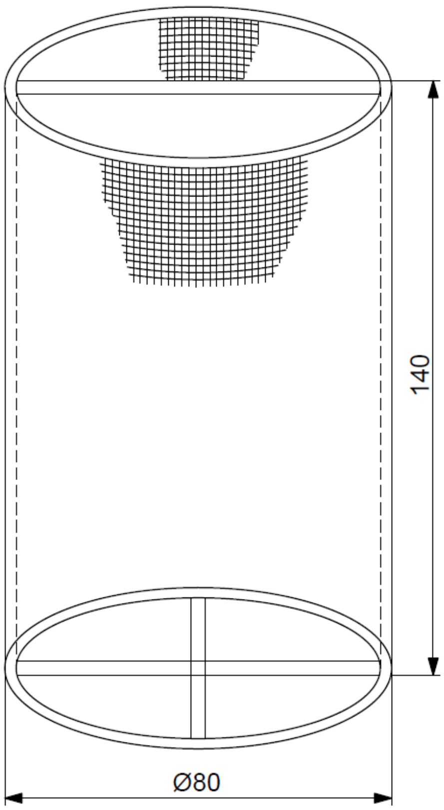


Figure 3.6 Schematic of mesh basket and picture of mesh basket used

Both the baskets are suspended into the solution for (17 ± 0.5) hours ensuring that at minimum cover of 20mm is achieved. After immersion, the baskets are removed from the solution and drain for (2 ± 0.25) hours before being placed into the oven 110°C ± 5°C for (24 ± 1) hours. Both specimens were then removed and cooled to ambient temperature for (5 ± 0.25) hours before repeating the cycle. The test requires 5 cycles to be conducted with each cycle lasting 48 hours. Once the final cycle has been completed, the specimens are rinsed with water and sieved using a 10mm sieve then put back into the oven and dried until a constant mass is reached.

The magnesium sulphate value (MS) was determined as:

$$MS = 100\frac{(M_1 - M_2)}{M_1} \quad (6)$$

Where M_1 = initial mass of specimen, to the nearest 0.1g;

M_2 = finial mass of specimen retained on 10mm sieve, to the nearest 0.1g.

3.5.6 Los Angeles Test Method (LA Test) for Resistance to Fragmentation

Conforming with BS EN 1097-2: 2010, the Los Angeles test method is used to determine an aggregates resistance to fragmentation. A specimen weighing 5000g is placed into a rotating steel hollow drum (Figure 3.7) with a ball load equal to 4690g to 4860g (load distributed over 11 spherical steel balls). The test specimen must pass a 14mm aperture size sieve and be retained on a 10mm aperture size sieve, with and intermediate complying with one of the two following restrictions:

- Between 60% and 70% passing a 12.5mm sieve, or
- Between 30% and 40% passing a 11.2mm sieve.

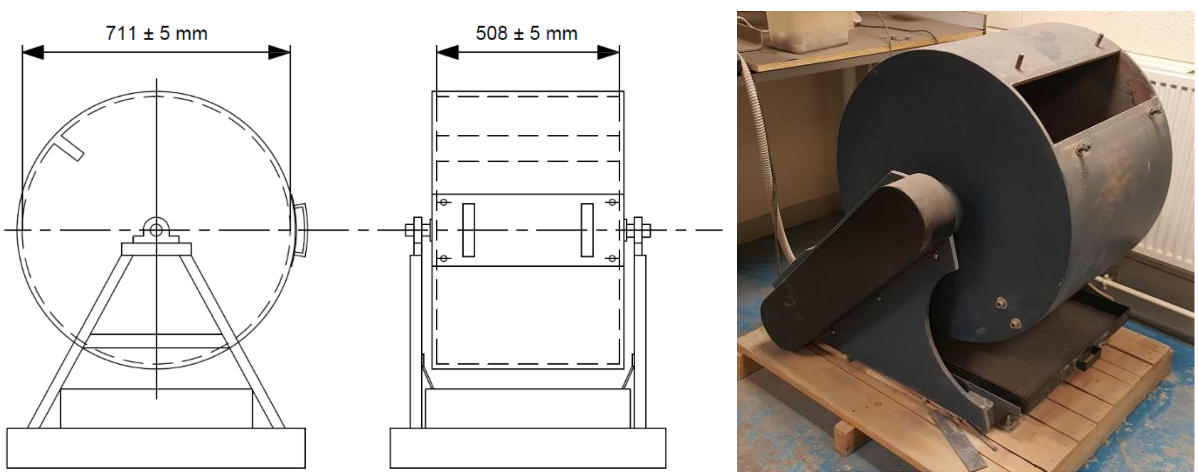


Figure 3.7 Schematic of LA testing drum and picture of the LA drum

Once the specimen is weighed out and the conditions for grading have been met then the specimen is placed into the drum with the ball load and the lid bolted down. The drum rotates for 500 revolutions at a constant speed of 31 min^{-1} to 33 min^{-1}. After the test has finished, the specimen was emptied onto a tray located below the drum and the ball load is removed. The specimen is then washed, dried and sieved using a 1.6mm aperture size. The Los Angeles coefficient (LA) is determined by:

$$LA = \frac{5000 - m}{50} \quad (11)$$

Where m = mass retained on 1.6mm sieve, in grams.

3.5.7 Using Automated Air Void Analysis

The use of air void analysis is a method to quantify the microstructural properties of a concrete sample, thus, its durability during freeze-thaw. BS EN 480-11 and ASTM C457 specify that a concrete sample is analysed under a microscope to look at its air void parameters. This consisted of an operator spending anything up to six hours to analyse a 100x100mm sample creating several issues such as human error when void sizes are being counted. Errors such as these are reduced considerably when the test is conducted using an automated microscope controlled by a computer. Furthermore, the time taken to conduct the test is reduced to approximately 20 mins meaning that for every sample analysed using the manual, 18 samples can be analysed using the automated method. Moreover, the standards used to designate the parameters (BS EN 480-11 and ASTM C457) can be alternated. Therefore, for the duration of the project automated analysis will be used to quantify the air void parameters.

Air void analysis is a method to determine air void characteristics within a concrete specimen. The method uses a microscope which traverses a specimen, identifying air voids and determining parameters such as air void size and distribution, frequency, spacing factor, specific surface and the hardened air content. The air void analysis of concrete was carried out uses a RapidAir 3000 Microscopic Analyzer (Figure 3.8). The test complied with BS EN 480-11:2005 and ASTM C 457:2009.

Figure 3.8 RapidAir 457 Microscopic Analyzer equipment

3.5.7.1 Sample Preparation

Two 100mm cubes were cast and placed into a water bath to cure for a minimum of 7 days before a 20mm slice is taken from the centre of the cube and cleaned for analysis. Once washed and cleaned the samples are then polished to produce a smooth shine on the surface preventing any impurities or crevices to be picked up by the microscope. Polishing takes approximately 1 hour per slice as 4 polishing grit grades (320, 600, 800 and 1200) are used to create the required shine. The specimen was then thoroughly cleaned to avoid any material remaining in the pores influencing the results. Ensuring the specimen is smooth and even, the test surface of the slice is completely blackened. Afterwards the application of barium sulphide (white powder) to the concrete produces a contrast for the microscope to clearly analysis the specimen (Figure 3.9).

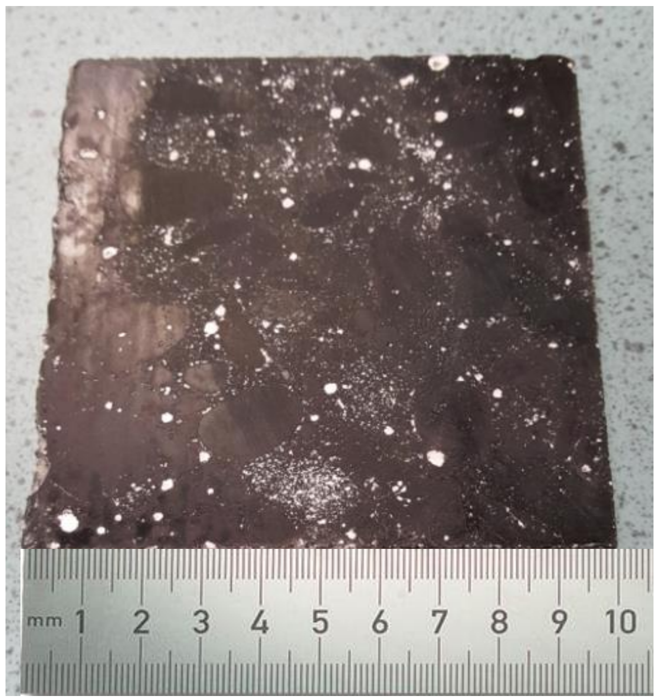


Figure 3.9 Samples for the air void analyser with a blackened surface and white powder ton contrast the voids against the flat surface

3.5.7.2 Standardized Testing Procedure for Air Void Analysis

Originally, determination of the air void characteristics was done by means of using a manually controlled microscope moving the specimen and calculating the characteristics. This method is in accordance with BS EN 480-11. Specimens were placed on to a cross-traverse table so that the traverse lines followed were running parallel to the upper surface of the concrete. A minimum traverse distance of 1200mm per specimen, totalling 2400mm. Three sets of four lines which are laid out in the uppermost, lowermost and central regions of the sample with each of the four lines in each set are spaced 6mm apart as illustrated in Figure 3.10.

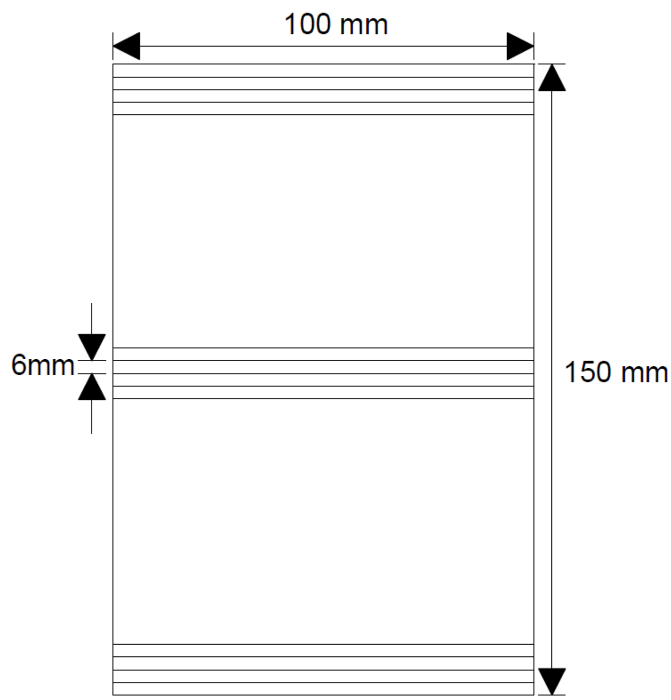


Figure 3.10 Layout of the traverse lines

The specimen moves along the table whilst the surface of the concrete is viewed through a microscope at a magnification of 100 ± 10x. Throughout the course of the testing, the magnification was not changed as this would affect the results.

As the test commences, the two screws used to move the table also provide separate measurements for the total distance travelled across the solid areas of the surface (T_s) and any voids encountered (T_a). The summation of the two results will give the total distance the traverse travelled (T_{tot}). Furthermore, the pore size distribution and the size of the micropores can also be determined with the number of chords generated by the crossing of the traverse lines with air voids. However, if it is discovered that, even with adequate grinding of the samples, that there are broken voids on a traverse line then the completed circular section is to be used for calculating the chord length as shown in Figure 3.11.

1 – Traverse line

2 – Zero chord length (l)

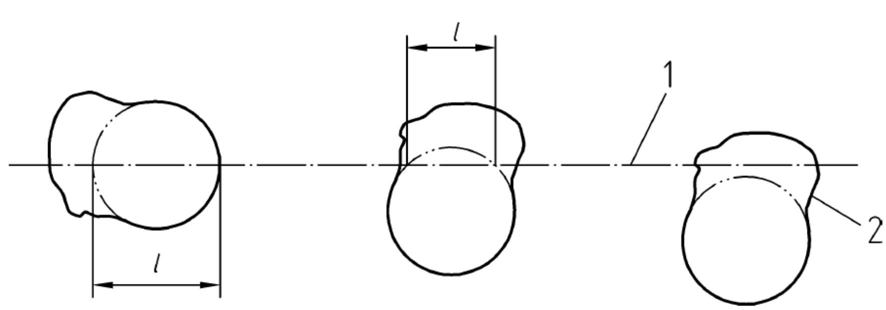


Figure 3.11 Estimating the chord length, l is used to mark broken edges

3.5.7.3 Using the Automated Analyzer

The automated air void method allows for samples to be read in a short period of time rather than taking several hours. The automated method conforms to ASTM C 457:2009 in that the setup of the instrument follows the guidelines laid out in this standard.

The process begins by placing the concrete slice into the clamp. When the program is opened, the window displays two images from the camera; the one on the left is real image that the camera reads and the image on the right displays what is known as the raw image. This is the processed image highlighting the voids in the sample and displaying them as green marks (Figure 3.12a). Both images coincide with one another as the camera moves from point to point.

The program starts by prompting the user to decide on which method to use to determine the air void characteristics (Figure 3.12b). For this project the linear traverse method was used using the European standard, BS EN 480-11 (Figure 3.12c). It should be noted that although the selection of the European standard is available, the method does not comply with BS EN 480-11. The program is setup up with the European parameters (Table 2.11 in Chapter 2) the execution of the program adheres to ASTM C 457. However, there is an option to carry out the BS EN 480-11 method (option below standard selection in Figure 3.12c) that can carry out the test method.

The next window prompts the user to enter the percentage of paste in the sample (Figure 3.12d). The paste content is determined by calculating the volume of the hardened paste content, cement binder and water, expressed as a percentage of the total volume. Once entered, the program requires the traverse length (e) to which the camera moves along. This value is determined by the aggregate size used in the concrete. ASTM C 457 outlines values along with transverse lengths depending on the size of coarse aggregate used.

The program requires the size of specimen and the area size to be traversed (Figure 3.12f). It is difficult to traverse the entire 100 mm^2 surface area due to the rough edges from the saw cut. A smaller traverse area is inputted into the program to prevent the inclusion of blank space in the output (Figure 3.13).

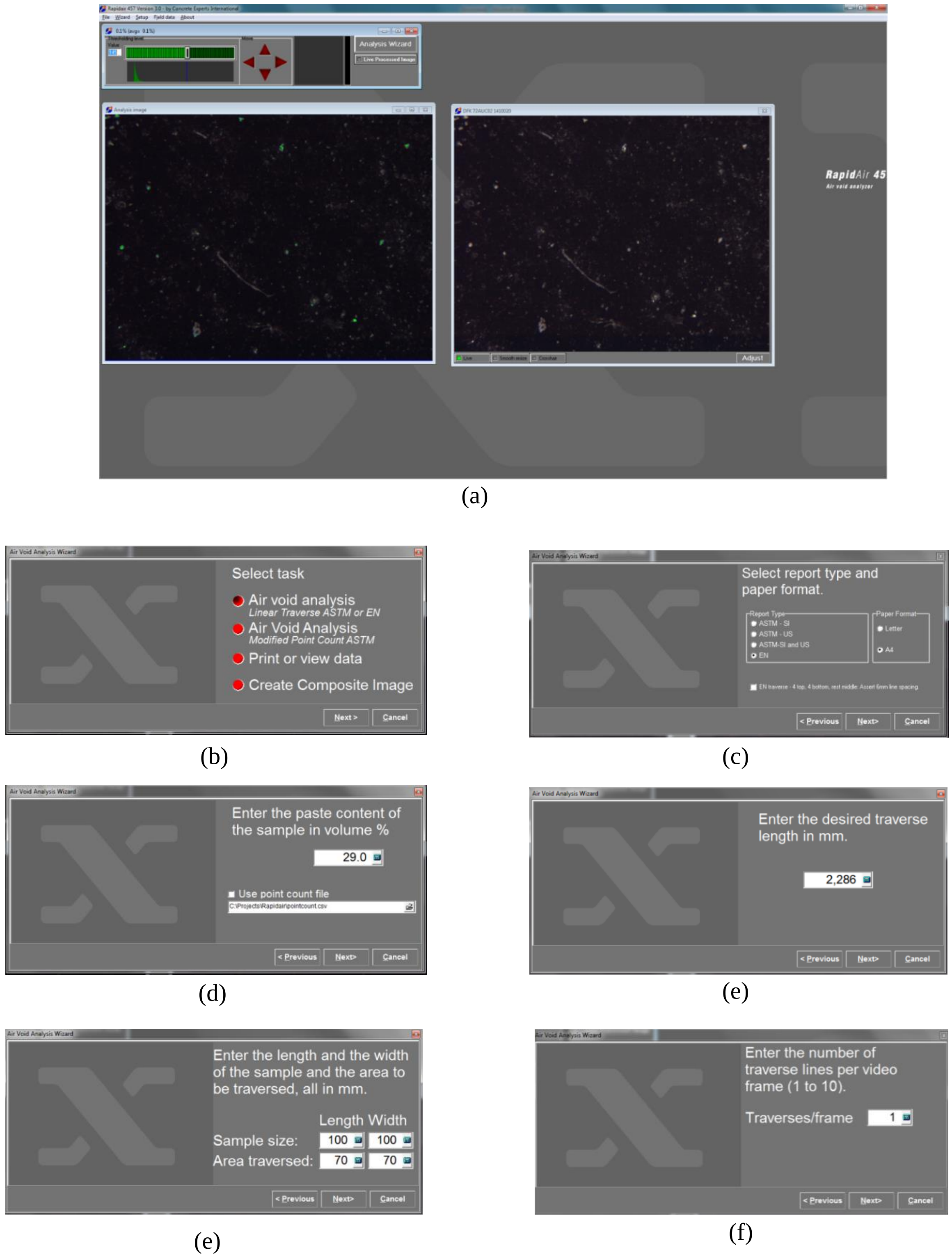


Figure 3.12 (a) Two windows depicting a raw image (white) and a processed image (green) (b) Selection for the analysis undertaken (c) Selection of standard which the analysis will adhere to (d) Input for paste content (e) Window prompting for traverse length (f) Window requiring specimen size and area to be traversed (g) Selection of probe lines

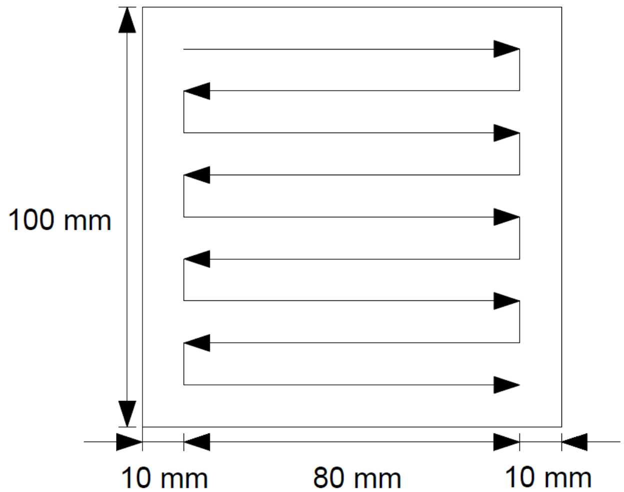


Figure 3.13 Diagram depicting the path of the air void analyser when using the linear traverse method

The remaining step before the analysis is carried out is to determine the number of probe lines to be used (Figure 3.12g). Probe lines determine how the microscope will divide up the specimen for analysis (Figure 3.14). Once the setup is complete, the specimen is then clamped into place ready to be analysed.

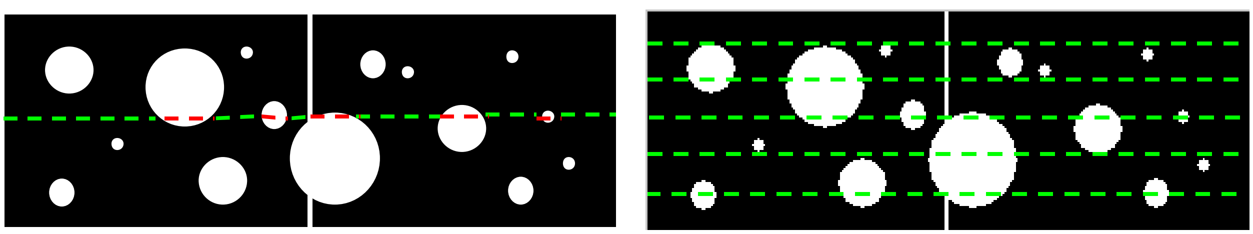


Figure 3.14 Illustrations depicting various probe lines used (Germann Intruments, 2005)

The running time is approximately 20 minutes though this time can vary depending on the traverse length and the number of probe lines used. The end result is an Excel spreadsheet with all the results including the bubble size and spacing and the spacing factor.

3.5.8 Test Method for Surface Salt Scaling (CEN/TS 12390-9)

3.5.8.1 Sample Preparation

The method outlines a specific procedure so that the test can produce accurate results over a range of concretes with varying cementitious materials that have been incorporated. The freeze-thaw test method for scaling was used to investigate a concrete's durability during cyclic temperatures.

The specimens were cast into 150x150x150mm cubes moulds, they were covered with damp hessian and left for 24 hours. Once the cubes were removed, they were transferred to a water, having a temperature of 20°C ± 2°C, where they remained for 7 days. On removing the cubes from the tank, the were dried with paper towels and moved into a temperature-controlled climate chamber maintaining a temperature of 20°C ± 2°C and a relative humidity of 65% ± 5% for a period of 14 days.

At 21 days old, the cubes are removed from the conditioning chamber and cut; firstly a 25 mm slice is taken from the end of the specimen, perpendicular to the top surface. Secondly, a 50 mm slice is taken from the from the remainder of the specimen meaning that the test surface will be from the centre of the concrete cube as shown in Figure 3.15.

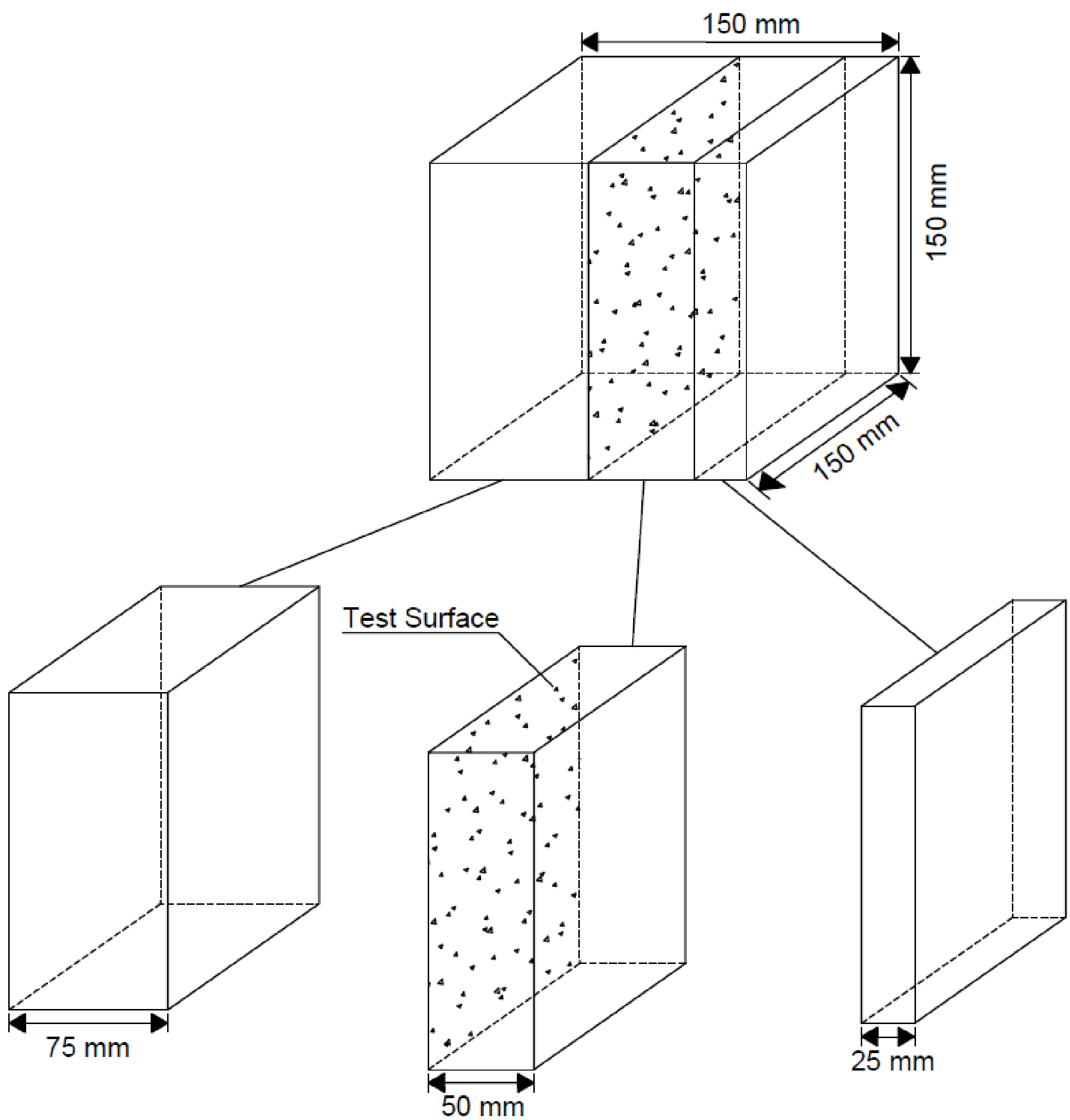


Figure 3.15 Diagram showing 50 mm slice and the adjusted cube centre

When the relevant cuts have been made the specimen, slice is immediately placed back into the climate chamber for another 4 days. Then, a rubber sheet is glued to the sides and base of the slice ensuring that the test surface is left exposed. The samples are put straight back into the conditioning chamber for a further

3 days allowing the sealant to dry, preventing any leakages. At 28 days old, a 3 mm deep layer of de-ionised/distilled water is poured on top of the test surface whilst the cubes are still in the chamber for a further 3 days ensuring that a temperature of 20°C ± 2°C and a relative humidity of 65% ± 5% is maintained. During this three-day period the cubes were checked daily to ensure that there was enough water on top so that the cubes could be saturated as much as possible.

When the cubes have reached 31 days old, they were ready to be placed in the freeze-thaw chamber. Before being placed in the chamber, the de-ionised/distilled water is removed from the surface and replaced with 3% concentration sodium chloride (NaCl) solution. Figure 3.16 depicts a sample which has been insulated and fully prepared to go into the chamber.

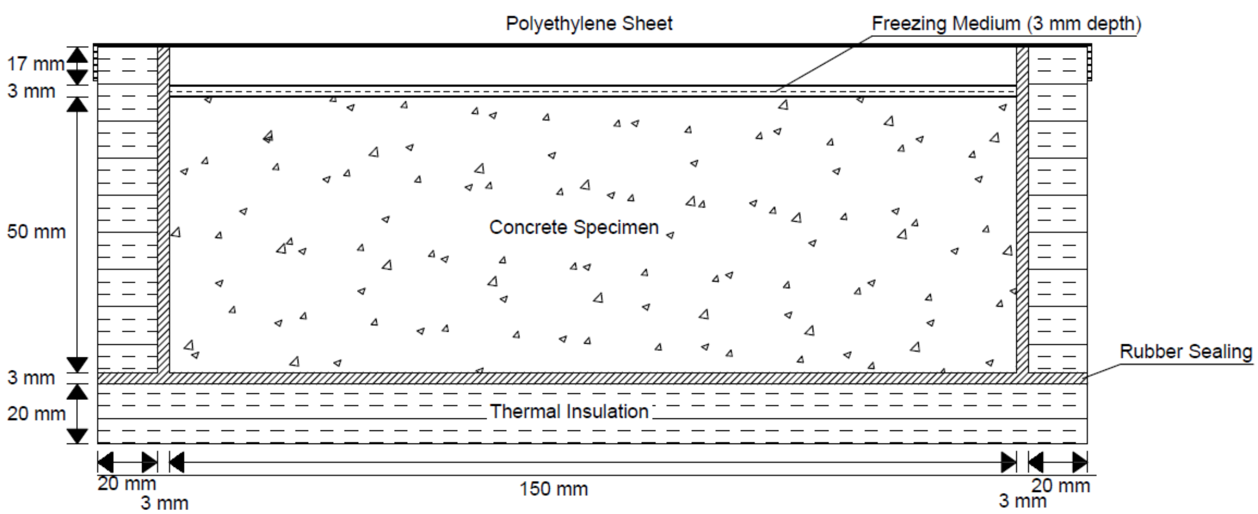


Figure 3.16 Cube setup for freeze-thaw testing to CEN/TS 12390-9

3.5.8.2 Testing Procedure

CEN/TS 12390-9 is carried out by placing the concrete samples into a freeze-thaw chamber for a total of 56 cycles or 56 days (one cycle is equal to 24 hours). As shown in Figure 2.20, the temperature ranges from +24°C to -22°C (these are the maximum and minimum temperatures of the envelope). In order to determine the damage caused by freeze-thaw, the samples are removed at intervals and the scaled material is removed from the testing surface. These intervals are 7, 14, 28, 42, and 56 cycles. Once the scaled material is removed from the sample, fresh salt solution is poured on top and the samples are placed back into the chamber (BSi, 2016).

The best method for removing the scaled material from the specimen is by using a fine bristle brush and spray water bottle filled with tap water. The material is removed into a container whereby the material is filtered (only required if small quantities of scaled material is gathered) so that all material can be collected.

Following on from this, the material is oven dried and weighed. The cumulative mass after n cycles ($m_{s,n}$) is calculated as:

$$m_{s,n} = m_{s,before} + \left(m_{v+s(+f)} - m_{v(+f)}\right) \quad (9)$$

Where $m_{s,\,before}$ = the cumulative mass of the dried scaled material calculated at the interval before;

$m_{v+s(+f)}$ = the mass of the container and filter (if used) containing the dried scaled material;

$m_{v(+f)}$ = the mass of the container and filter when empty.

A value for the cumulative mass of dried material is calculated after a total of 56 cycles is then used to determine the total mass of scaled material of the test surface after n cycles (S_n) in kg/m^2:

$$S_n = \frac{m_{s,n}}{A} \,.\, 10^3 \quad (10)$$

Where: $m_{s,n}$ = the cumulative mass of the dried scaled material after n freeze-thaw cycles;

A = Area of the specimen.

3.6 Lightweight Aggregate Concrete – Phase 1b

During this project, samples of concrete containing lightweight aggregate from a structure were analysed and tested to understand why pieces of the structure were spalling off and yet the reinforcement at different parts were looking like new. Cores were analysed using the air void equipment to find that due to the high porosity of the aggregate, the hardened air content was very high (>10%). This led to the idea that lightweight aggregate provides a natural protection when the concrete is subjected to freeze-thaw attack. Furthermore, according to BS 8500-1, lightweight aggregate has the capability to withstand freeze-thaw attack in the presence of de-icing salt (XF4) meaning that it has the same capacity to withstand freeze-thaw attack as C28/35 with air and RC40/50 XF. To test this, a series of concretes were cast to determine durability against one another for strength and freeze-thaw resistance. The mix designs, fresh properties and strength results are shown in Table 3.14 and Table 3.15 respectively.

Since lightweight aggregate is not a common aggregate used in construction, both CEM I and CEM III/A were tested to investigate whether the addition of replacement material would have any effect on the performance. Freeze-thaw performance was also conducted as described in CEN/TS 12390-9. Freeze-thaw was not the only possibility for the spalling concrete, several different theories were considered mainly freeze-thaw and chloride ingress. Chloride ingress affects mainly the reinforcement causing it to oxidise and expand exerting pressure on the concrete before spalling off. However, this was not the case for the areas that were being investigated. The reinforcement was like new, so it was considered that the aggregate absorbed the chlorides from the solution preventing oxidation of the steel.

Table 3.14 Mix designs for concrete containing lightweight aggregate

Mix Code	Target Strength, MPa	Constituent Material, kg/m³								w/c Ratio	Admixture %[1]	
		Cement Binder			Water	Aggregates						
		CEM I	GGBS	Salt		0/4	6/14	4/10	10/20		SP	AEA
C1	C28/35	144	177	-	182	750	-	370	740	0.57	0.8	-
C2	C28/35 with air	169	207	-	181	714	-	367	734	0.48	0.8	0.41
C3	RC40/50	188	229	-	151	725	-	377	755	0.36	1.0	-
LWA1	LC40/44	458	-	-	172	463	759	-	-	0.38	0.42	-
LWA2	LC40/44	206	252	-	167	462	758	-	-	0.37	0.42	-
LWA3	LC40/44 with Cl	204	249	18	165	458	751	-	-	0.37	0.42	-
LWA4[1]	LC40/44	458	-	-	172	463	758	-	-	0.38	0.42	-
LWA5[1]	LC40/44	206	251	-	167	462	757	-	-	0.37	0.42	-
LWA6[1]	LC40/44 with Cl	204	249	18	165	458	751	-	-	0.38	0.42	-

1) Lightweight sand used rather than natural glacial sand

Table 3.15 Fresh properties and compressive strength results of concrete containing lightweight aggregate

Mix Code	Slump, mm	Fresh Air Content, %	Compressive Strength, MPa			
			3 days	7 days	28 days	COV, %[1]
C1	120	1.4	16.2	26.6	38.1	0.66
C2	90	5.3	15.5	23.7	34.6	3.83
C3	120	1.5	23.0	34.4	49.6	0.98
LWA1	125	2.9	43.4	48.2	55.5	2.38
LWA2	200	3.9	27.3	37.3	50.1	1.85
LWA3	125	3.7	35.8	46.4	51.6	2.45
LWA4	190	4.9	34.1	37.7	50.0	0.90
LWA5	175	5.5	23.6	33.3	41.3	6.08
LWA6	100	5.0	38.6	42.0	46.0	5.34

(1)Coefficient of Variation for the compressive strengths at 28 days only

3.6.1 Testing Whether Salt Saturation Provides Protection during Freeze-Thaw Attack

A series of test were conducted to determine how the aggregate protects the reinforcement from environmental deterioration. Aggregate was put through a series of wetting and drying cycles to simulate the external environment. This was conducted by placing approximately 500g of aggregate into 3% NaCl solution for 24 hours before removing from the solution and left to dry for 24 hours. This cycle was carried out 10 times to allow adequate salt mass to gather in the pores of the material. The material was then put through the freeze-thaw test for aggregates (BS EN 1367-1) and the results compared to the material with no salt.

3.6.2 CT Analysis of Aggregate

Using the micro-CT scanner (Figure 3.17), the micro-structure of aggregate was analysed to determine the porosity and pore size distribution. Also, 40x40x40mm cubes were cast from mortar using both CEM I and CEM III/A (50%) to visualize the internal air void structure and whether the distribution of the voids is like that of the lightweight aggregate.

Figure 3.17 Micro-CT scanner used to visualize the internal structure of aggregate, mortar and concrete

3.7 Influence of Air Content of Aggregate on the Total Air Content of Concrete

During this project, concrete has been analysed using the RapidAir 457 air void analysis equipment to determine the hardened air content of concrete. However, when it comes to analysing concrete with porous aggregate then the air content becomes high as a result of the porosity of the aggregate.

Determining the influence of the aggregate's porosity, lightweight aggregate was cast into resin to prevent any bubbles forming in the material and allowing only the air content of the aggregate to be scanned. This was done by blacking out the resin after the white powder had been applied (ensuring complete blackout) then running it through the analyser and calculating the air content of the aggregate. This would determine how much of the air content is affect by the voids in the aggregate and from that it is then possible to manipulate the air content equation to consider the addition of the extra air content.

3.8 Influence of Fly Ash Type on Freeze-Thaw Durability

Fly ash is difficult to predict when any testing is conducted as each batch can vary in its properties such as its carbon content or fineness so when concrete containing fly ash is cast each sample can also very in terms of its structural properties including durability aspects. This section looks at the effects of different fly ashes in concrete that are both non-air and air entrained to determine the variability not only between each fly ash but also each cube from the same batch varies too. All the CEM II/B-V mixes have the same mix design with the only variable being the type of fly ash used. Table 3.16 outlines the fresh properties and the compressive strengths for the CEM II/B-V concretes used.

Table 3.16 Admixture content, fresh properties and compressive strengths of concretes containing different fly ashes

Mix Code	Admixture Content, %[1)]		Fresh Properties		Compressive Strength, MPa			
	SP	AE	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %[2)]
Non-Air Entrained								
DFA1	0.68	-	120	1.5	23.7	27.6	39.4	1.83
DFA2	0.56	-	120	1.5	21.4	27.1	39.8	2.53
DFA3	0.37	-	115	1.2	21.1	25.7	37.7	1.99
DFA4	0.37	-	120	1.1	20.6	26.7	36.2	0.73
DFA5	0.37	-	125	1.2	21.5	26.2	37.8	1.31
Air Entrained								
DFA1A	0.62	0.57	100	4.7	24.2	29.2	36.4	4.39
DFA2A	0.48	0.57	120	4.9	22.4	25.7	39.1	3.18
DFA3A	0.31	0.57	100	4.4	22.4	27.2	38.1	3.11
DFA4A	0.31	0.57	110	4.6	21.5	27.1	36.2	2.19
DFA5A	0.31	0.57	115	4.7	22.7	26.9	37.5	2.85

[1)]% weight of total cement content
[2)]Coefficient of Variation for the compressive strengths at 28 days only

3.9 Compatibility of Different Admixture Types – Phase 2

In this section of the study, tests are to be carried out on various combinations of different admixtures in order to gauge what chemical reactions take place in the fresh state and during the hardening process. It has not identified if the mixing of admixtures causes any long-term effects on the concrete performance to withstand freeze-thaw so this study should aid in the investigation.

This study is carried out by comparing concretes with various admixtures against a control mix to determine if there indeed any long-term problems or advantages. Each of the concretes in Table 3.16 will be put through several tests (compression test, air void analysis and freeze-thaw) to compare the characteristics of each mix with the CEM I and CEM III/A control mix which is listed as reference concrete III in BS EN 480-1. For this study to be completed fully, a total of 12 mixes were produced shown in Table 3.17 and the admixture type, combination, quantity used along with the fresh properties and compressive strengths are shown in Table 3.18.

Table 3.17 Concrete mixes with various admixture combinations

Mix Code	Admixture Combo	Constituent Materials, kg/m^3						Admixtures
		Cement/Addition		Water	Aggregates			
		CEM I	GGBS		0/4	4/10	10/20	
AC1 (CEM I Control)	No Adm	355	-	190	740	375	750	See Table 3.18
AC2 (CEM III/A Control)	No Adm	160	195	185	740	375	750	
AC3	SP1	160	195	185	740	375	750	
AC4	SP2	160	195	185	740	375	750	
AC5	AE1	189	231	185	715	375	750	
AC6	AE2	189	231	185	715	375	750	
AC7	SP1+AE1	189	231	185	715	375	750	
AC8	SP1+AE2	189	231	185	715	375	750	
AC9	SP2+AE1	189	231	185	715	375	750	
AC10	SP2+AE2	189	231	185	715	375	750	
AC11	ACC+AE1	189	231	185	715	375	750	
AC12	VMA+AE1	189	231	185	715	375	750	

Table 3.18 CEM III/A (GGBS) mixes with various admixtures combinations, fresh concrete properties and compressive strength values

Mix Code	Admixture Type and Content, % wt of total cement							Fresh Properties		Compressive Strength, MPa			
	No ADM	SP 1	SP 2	AEA 1	AEA 2	ACC	VMA	Slump, mm	Air Content, %	3 Days	7 Days	28 Days	COV, %[1)]
AC1 (CEM I Control)	0.0	-	-	-	-	-	-	60	0.8	33.7	36.2	46.4	1.02
AC2 (CEM III/A Control)	0.0	-	-	-	-	-	-	35	1.0	22.5	28.2	40.1	3.68
AC3	-	0.48	-	-	-	-	-	140	1.4	20.1	29.9	41.1	2.97
AC4	-	-	0.39	-	-	-	-	180	2.0	20.7	27.0	39.1	3.44
AC5	-	-	-	0.48	-	-	-	45	4.6	15.7	21.8	32.4	2.78
AC6	-	-	-	-	0.52	-	-	50	4.0	16.8	23.1	35.7	2.35
AC7	-	0.41	-	0.48	-	-	-	120	4.7	19.1	28.6	42.2	1.09
AC8	-	0.41	-	-	0.52	-	-	150	4.2	23.4	29.9	40.6	0.71
AC9	-	-	0.33	0.48	-	-	-	140	4.7	22.5	28.5	38.7	2.88
AC10	-	-	0.33	-	0.63	-	-	125	4.2	24.4	33.7	46.6	6.09
AC11	-	-	-	0.48	-	0.33	-	30	4.4	19.2	27.4	38.2	2.00
AC12	-	-	-	0.48	-	-	0.45	25	4.4	23.8	29.7	43.7	2.32

3.10 Deriving an Equation to Calculate the Rate of Deterioration

Deterioration of concrete is determined by the environmental conditions in the structure's location. Environmental factors such as chloride ingress and carbonation each can be pre-determined and designed into the concrete mix through their respective equations. Freeze-thaw, however, does not have this type of equation due to its unpredictability and inability to repeat the test and achieve the same result twice. During this study it shall be attempted to derive an equation for the rate of deterioration for a concrete sample to then calculate the point of which an *Unacceptable* scaling rating is achieved (>1.0kg/m^2) or determine the cycle where scaling becomes negligible.

Using the data collected from the total mass loss from scaling, a graph is produced depicting the increase in mass loss over the number of cycles. From this the rate of deterioration can be determined for this sample (only) and the equation used can determine the approximate cycle number where the total scaling loss will pass the limit of 1.0kg/m^2 (*Unacceptable* scaling rating) as detailed in CEN/TS 12390-9 and SS 137244.

The CEN test value is calculated through the cumulative mass of scaled material lost during the test stage whereby the final calculation to determine the cumulative loss is not undertaken until the 56 cycles is complete. Therefore, the graph depicting the material loss will only increase over the cycle time until a plateau point is reached where negligible scaling occurs. As the graph is progressively increasing then a logarithmic best fit line can be used to idealise the increase in scaling loss and produce an equation of the line which can be used as the rate of deterioration for that concrete specimen.

Figure 3.18 shows the scaling loss for a test concrete depicting the continual increase in the scaling loss at each test interval. Applying a best fit line shows a progressive curve from the first test cycle (7 cycles) until the last (56 cycles). It should be noted that for the equation for the line to be produced, the first point must be taken from the first point as the logarithmic curve does not pass through zero. Equation shows the rate of deterioration for the sample.

$$y = 0.2967\ln(x)$$

Where the gradient of the line (*m*) is the rate of deterioration (m = 0.2967*)* and (*x*) is the number of cycles. The rate of deterioration is measured as:

$$kg/m^2/cycle$$

Given that the results show that the cumulative mass of scaled material is constantly increasing then a logarithmic curve would provide the 'best fit' line. Had a logarithmic scale been used then a straight line would be observed. From the figure, it is seen that line of the graph does not start at zero as it is assumed that no scaling occurs at 0 cycles since the sample has not entered the freeze-thaw chamber.

Furthermore, the generic equation of the line shows *m* (the gradient) and *c* (y intercept) and in this case the logarithmic equation:

$$y = m\ln(x) + c$$

The y-intercept defines the point at which the line will cross the y-axis and this be positive or negative suggesting that material has already scaled before the test began (positive value) or the scaled material which was not lost has returned to the sample (negative value) until the line crosses the x-axis becoming positive and scaling loss begins.

Obviously, this cannot be true as it would mean during the first 7 cycles the sample somehow manages to regain scaled material not yet lost to freeze-thaw making the results very questionable. Therefore, the decision was made to disregard the y-intercept and focus on the gradient of the line which is deemed to be the rate of deterioration.

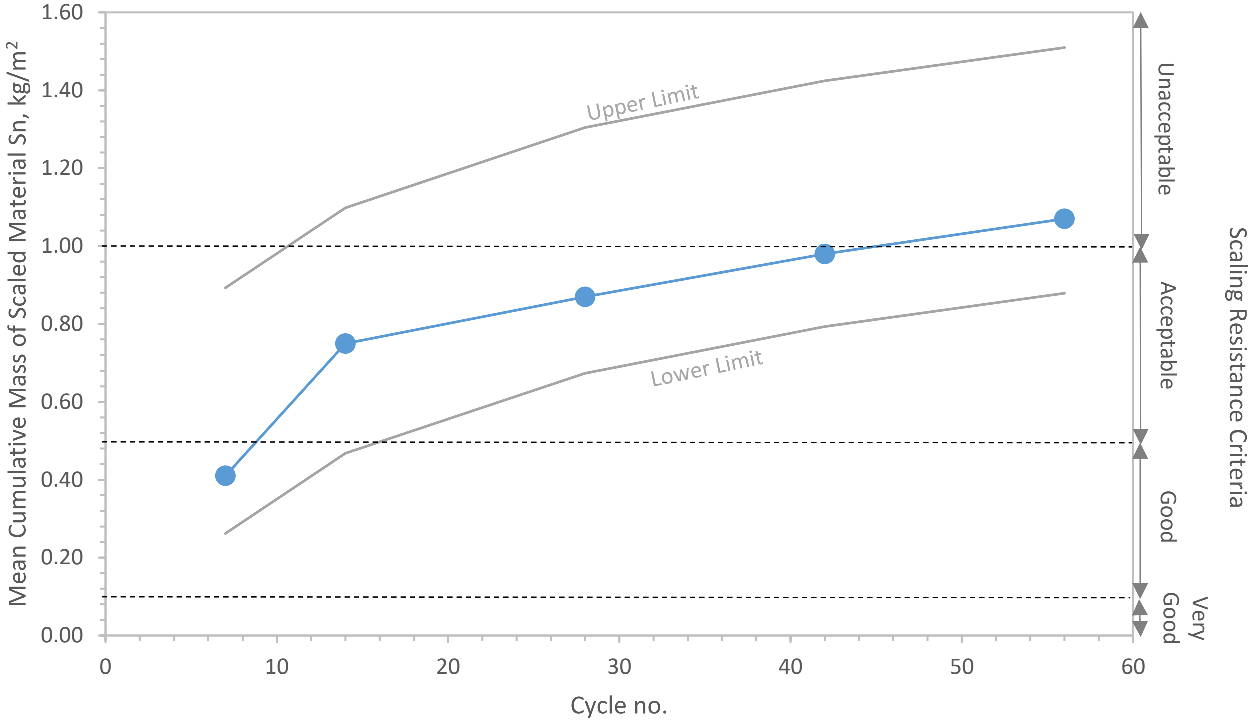


Figure 3.18 Scaling result for a non-air entrained CEM I concrete (M1) with a best fit lines to determine the rate of deterioration and the determine confidence limits for the sample

Table 3.19 comprises of a comparison between real data produced from the example above and the data calculated using the rate of deterioration equation. As shown, the initial 7 cycles define a much larger difference in the result of nearly 30% which related to the scaling loss on the surface where most of the material is lost. Afterwards, the difference averages out around 10% higher showing that for the calculated data it is going to be a conservative number when estimating the mass loss of scaled material. The difference between the test data and calculated, of 10%, can be a large difference in the results. However, the calculated data can be considered as a conservative overestimation without having conducted any testing, this way if the user was unable to test to the 56 cycles there can be a margin for error in the results. For an air entrained concrete, the calculated result is approximately 10% below the test data.

Whilst it is difficult to determine a tolerance to measure the margin of error with the results produced due to each mix having different variables and creating a standard percentage tolerance due to each mix having its own equation, it would be the simpler option to determine confidence limits (95%) to express an upper and lower limit for the equation which can be used as a measure for the calculated data when determining the approximate loss for later cycles ensuring that when future material loss is calculated, there is a known range the data will be within based upon the equation produced from the 56 cycle results . Figure 3.18 shows the confidence limits for the equation.

Table 3.19 Comparison between data determined using the freeze-thaw test method and those calculated using the rate of deterioration equation (y = 0.2967ln(x))

Cycle No.	**CEN Test Data, kg/m^2**	**Calculated Data, kg/m^2**	**Difference, %**
7	0.41	0.58	29.3
14	0.75	0.78	3.9
28	0.87	0.99	12.1
42	0.98	1.11	11.7
56	1.07	1.19	10.1

3.11 Modifying the CEN/TS 12390-9 Test Method to Suit the Current Climate – Phase 4

One of the focus points for this project is to assess the CEN/TS 12390-9 test method for freeze-thaw to determine if the preparation and the parameters set in the standards can be readjusted to better assess the British and European climates. The test set out in the standards has been shown to have a number of problems and a number of areas which can be improved, such as the salt concentration from the de-icing salts, the number of cycles, the temperature profile the cycles go through and the cube size. Moreover, when the cubes have finished the 56 cycles there is more damage under the surface than what there appears to be. Figure 3.19a depicts the extent of the damage (in comparison to their undamaged shape before the scaling test) on the surface after undergoing testing, whilst Figure 3.19b shows the damage beneath the surface which does not contribute to the final result.

3.11.1 The Addition of Surface Scaling from the Sides and Base

CEN/TS 12390-9 distinguishes how a concrete performs in freeze-thaw by a pass/fail result. Though the test only determines this through surface scaling of the test surface, it does not take into consideration the scaling of the base and sides of the specimen. Once the specimens had been subjected to 56 cycles, the rubber seal and sealant were removed from the concrete and any excess material was collected, dried and weighed to determine whether the addition of the extra scaled material would have an effect on the total cumulative mass of scaled material and if so how much by.

Figure 3.19 (a) Scaling damaged to the test surface and (b) damaged to the surfaces below the testing area

3.11.2 Testing the Freeze-Thaw Performance of a Concrete's Cast Surface

Once concrete has been cast, hardened and the mould removed, a smooth cast face is general produced depending on the required finish. Most of the laboratory testing conducted is on the better quality of concrete (freeze-thaw done on the internal concrete, Figure 3.15). This section looks at testing the cast surface for freeze-thaw performance as it is this surface which is exposed to the external environment. A 50mm slice is taken from the outside of a 150mm cube and turned upside down so that the cast surface is visible and tested to CEN/TS 12390-9 test method.

3.11.3 Salt Concentration

One aspect of the test method is varying the salt concentration applied to the samples. Typically, the samples have a saline solution that has a concentration of 3% which represents an approximation of the concentration in de-icing salts. Though in reality, the salt concentration is not constant when it has been spread. During the winter months, especially in the UK, the roads and pavements have de-icing salts daily, even two to three times a day meaning that with more applications of salt, the concentration increases.

Varying the salt concentration during the freeze-thaw test so that it closely represents the changing concentration on the roads. This is conducted by increasing the salt concentration of the solution from the standard 3% detailed in CEN/TS 12390-9 to 6%, 9% and 12% to determine the effects of a higher salt concentration. The increased solutions were tested on both air and non-air entrained concretes providing a representation of various freeze-thaw de-icing salt practices used by highways management teams.

3.11.4 Temperature Profile

For this study, two temperature variations were considered mainly aiming to identify the effects of reducing the maximum and minimum temperatures the specimens are subjected to. Profile variation 1 (V1) looks at reducing the maximum temperature by 10°C and increasing the minimum by 5°C (+5°C, -10°C). Where profile variation 2 (V2) looks to reduce the maximum temperature by 5°C and increase the minimum by 10°C (+10°C, -5°C).

3.11.5 Carbonation Study

This study was carried out to determine the effect of carbonation on concrete would be subjected to freeze-thaw deterioration. The study was tested in accordance with BS 1881-210:2012 for accelerated carbonation and CEN/TS 12390-9:2016 for freeze-thaw salt scaling. The process behind the study was to carbonate enough depth of the concrete to determine whether the concrete, when subjected to freeze-thaw, would perform better or worse.

Concretes were cast to produce a 40 MPa design strength using the maximum replacement content as described in BS 8500-1. The specimens used for this study were a 500x100x100mm prism as a control and eleven 150x150x150mm cubes. After 24 hours in the mould and covered in damp hessian, the concrete specimens were removed from their moulds and immediately placed into the curing tank for a further 27 days. On removal from the tank, specimens were air dried for 24 hours at 20°C in the laboratory.

Prior to the specimens going into the accelerated carbonation tank, four faces of the specimens were covered in 5mm of melted paraffin wax in three layers, leaving two longitudinal faces exposed. The test tank (Figure 3.20) had a continuous flow of 4% ± 1% (40000 ± 5000 ppm) CO_2, a temperature of 20°C ± 2°C and relative humidity of 55% ± 5% (Kandasami et al, 2012). The specimens were positioned in a way which allows air to circulate freely.

At set testing ages, a 50mm thick slice was split from the prism and a cube was split in half, both were then sprayed with a phenolphthalein solution. The split face was then divided into eight equal sections and the five central points on each side were measured, giving ten reading from the specimens in accordance with RILEM (1988) (Figure 3.21). Once a slice had been split, the exposed face on the prism was then resealed using melted paraffin wax to prevent any longitudinal carbonation from occurring.

Eleven 150x150x150mm cubes were cast to being with and would be used for different stages of the testing. Five were placed into the carbonation testing tank long with the prism to be tested at the various testing ages, three were placed into air tight polythene bags to minimise carbonation occurring and the final three were prepared as for the freeze-thaw test method (see above) and placed into the carbonation tank with the testing cubes and prism.

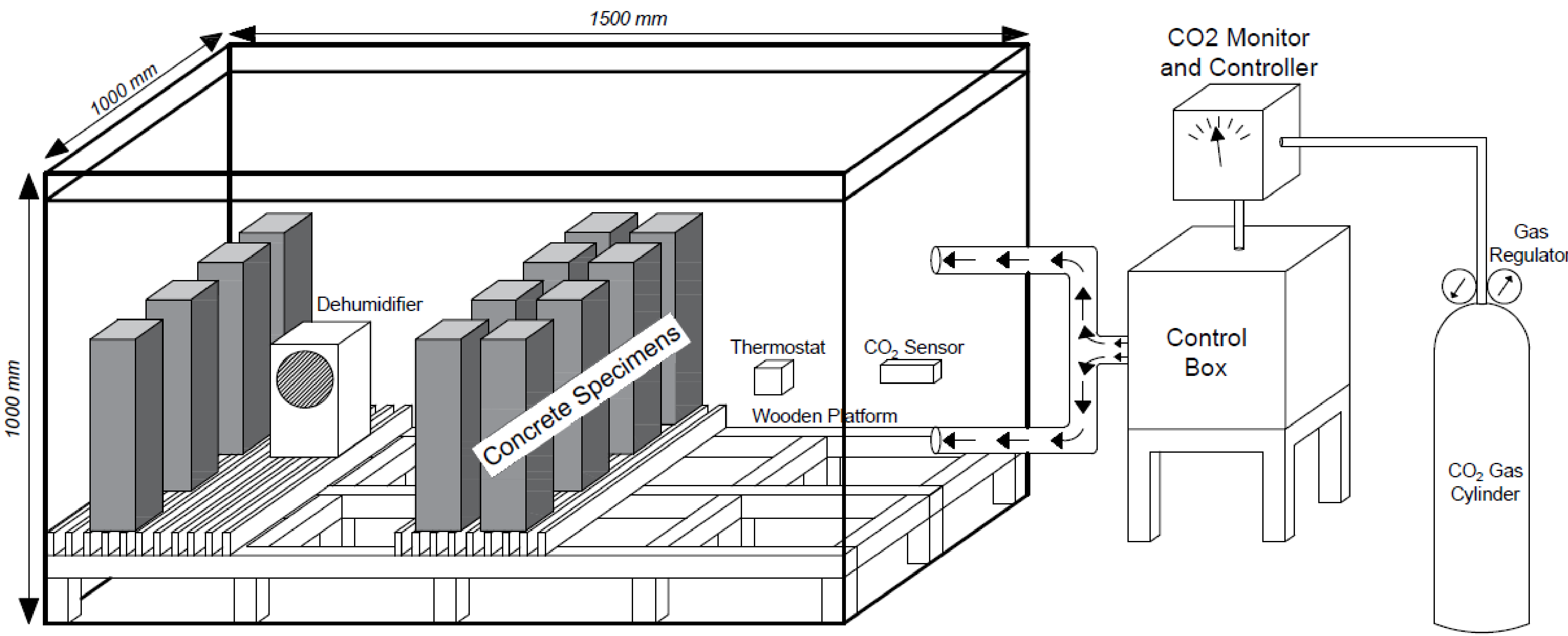


Figure 3.20 Schematic of accelerated carbonation chamber (Abbas, 2000; Newlands, 2001)

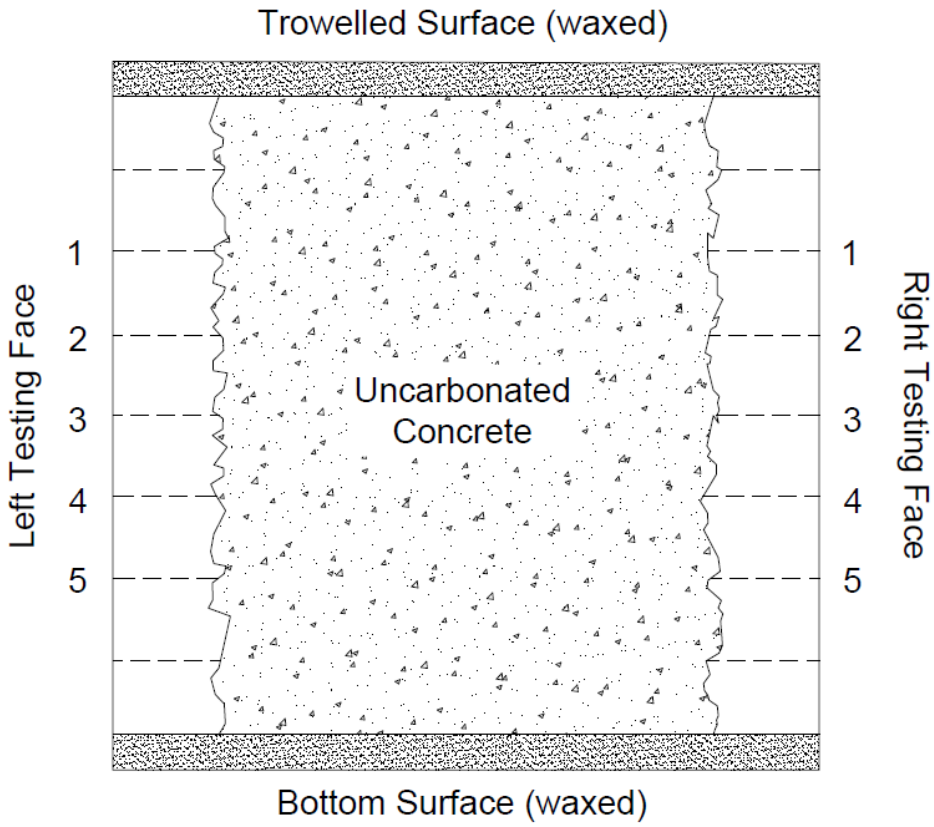


Figure 3.21 Measurement of carbonation depth of split surface

3.12 Summary of Chapter 3

This chapter reviewed the methodology implemented throughout the course of this research project to test the different materials, cementitious constituents and concretes. Following the standards, the various cement types, aggregates and admixtures used in the project testing the physical and chemical characteristics and how these influence the freeze-thaw resistance of the concrete mixes. A bulk mixing programme was designed to conduct a parametric study of the most available cements used in the construction industry, designing target strengths and air contents which are in accordance with BS EN 206 and BS 8500. The programme reviews the difference regarding the target strength for both non-air (Series 1) and air (Series 2) entrained concretes of different cement types. It also considers the influence of varied target air content (Series 3) and varied addition content (Series 4).

The procedure for analysing the samples to determine the air void characteristics was discussed highlighting the different parameters that are required for the analysis to be completed. Test methods were discussed to determine how lightweight aggregate would be tested to identify if lightweight is capable of withstanding freeze-thaw the same way air entrained, normal weight concrete does.

Modifications were outlined in this chapter as possible alterations for the freeze-thaw test. The temperature profile would be modified to consider other profiles would better suit the British and European climates along with the varying the salt concentration and the influence of carbonation on the freeze-thaw resistance.

Chapter 4
Quantifying the Air Void Characteristics of Different Concrete Mixes

4.1 Introduction

Concrete's structural properties define how well the concrete will endure structural loading and durability aspects whilst the members are in operation. The same can be said for the microstructural properties when it comes to freeze-thaw durability. Increasing the design strength or including air entrainment in the concrete will aid in the freeze-thaw resistance. However, what has not been fully considered is the interactions and formations of the microstructural voids during the fresh state and what is formed in the paste in the hardened state. Moreover, what physical and chemical interactions occur when not just CEM I is used but rather other cement types in varying replacement quantities.

Using automated air void analysis, the air void characteristics such as the spacing factor, specific surface, void frequency, average chord length and air content can be determined to identify which of the output parameters influence the microstructure of the concrete. Simply using the spacing factor as a measurement of whether a concrete has the capacity to withstand freeze-thaw attack is not enough, hence, using several the characteristics together to determine how well a concrete would potentially tolerate freeze-thaw attack.

4.2 Air Void Characteristics of Laboratory Concretes (Phase 1)

As stated in Chapter 3, several different concretes were designed and cast to determine various properties and durability aspects whilst changing the target strength, air content and cement replacement content. Two cubes from each mix were measured to determine the air void characteristics in accordance with BS EN 480-11.

4.2.1 Air Void Characteristics of Non-Air and Air Entrained Concretes (Series 1 & 2)

Initially, design mixes with different target strengths (20-60 MPa) included both non-air entrained (Series 1) and air entrained concretes (Series 2). These were designed to represent the concretes that are in typical UK concrete construction. Figure 4.1 to Figure 4.4 compare the air content of the fresh and hardened concretes and Table 4.1 to Table 4.4 show the air void parameters for the hardened concrete, calculated by the air void analyser for CEM I, CEM II/B-V, CEM III/A and CEM II/A-L concretes.

As shown in the figures, there is defined grouping of the non-air and air entrained concretes where the air entrained remain with the 4.5% ±1.0% tolerance. Whereas the non-air entrained results were more dispersed as these are more difficult to ensure a reduction in the air content as continual vibration of the sample will cause segregation (Neville, 1995).

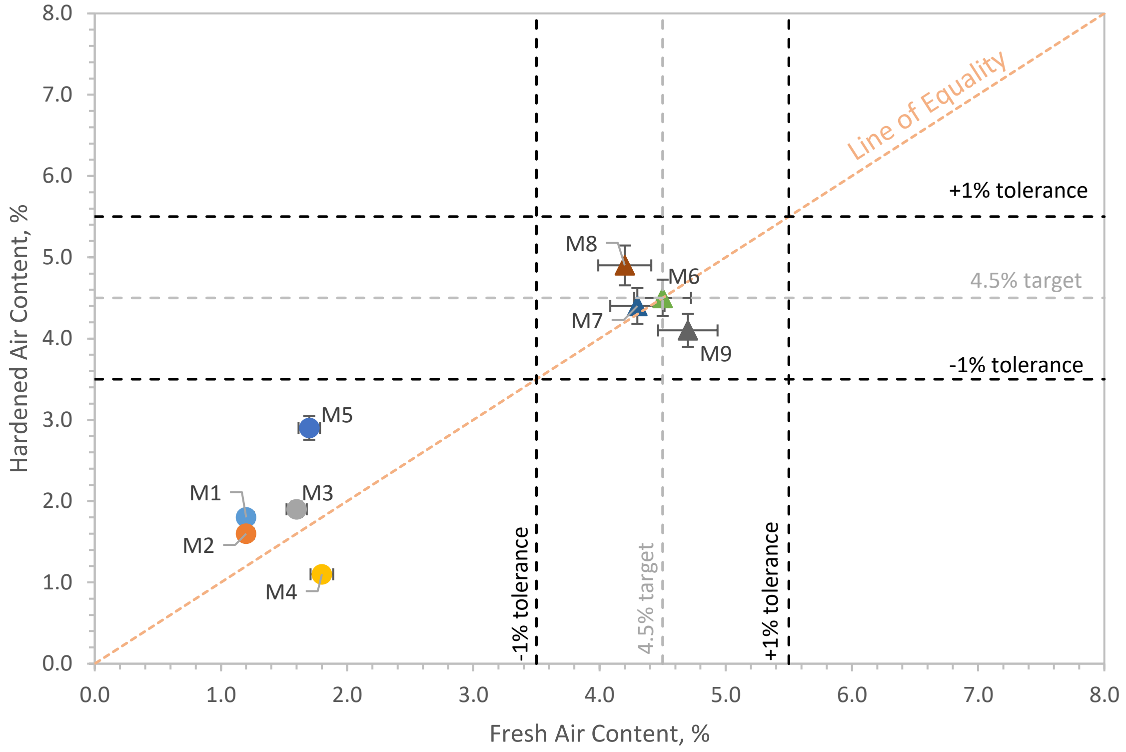


Figure 4.1 Comparison of air content measured in the fresh and hardened concrete for CEM I concretes with a line of equality

Table 4.1 Air void parameters for CEM I determined using the automated air void analyser

Mix Code	Air Content (Fresh), %	Air Content (Hardened), %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	[1)]Micro Air Content, %
Non-Air Entrained							
M1	1.2	1.8	0.084	81.19	0.352	0.051	1.2
M2	1.2	1.6	0.072	98.79	0.405	0.041	1.1
M3	1.6	1.9	0.068	106.62	0.464	0.040	1.4
M4	1.8	1.1	0.089	122.37	0.337	0.039	0.6
M5	1.7	2.9	0.081	74.84	0.551	0.054	2.0
Air Entrained							
M6	4.5	4.5	0.076	58.78	0.665	0.069	2.8
M7	4.3	4.4	0.084	56.31	0.616	0.071	2.9
M8	4.2	4.9	0.053	93.93	1.109	0.045	3.4
M9	4.7	4.1	0.097	55.66	0.550	0.073	2.3

1) Microair content is the total air content for void sizes <300µm in diameter

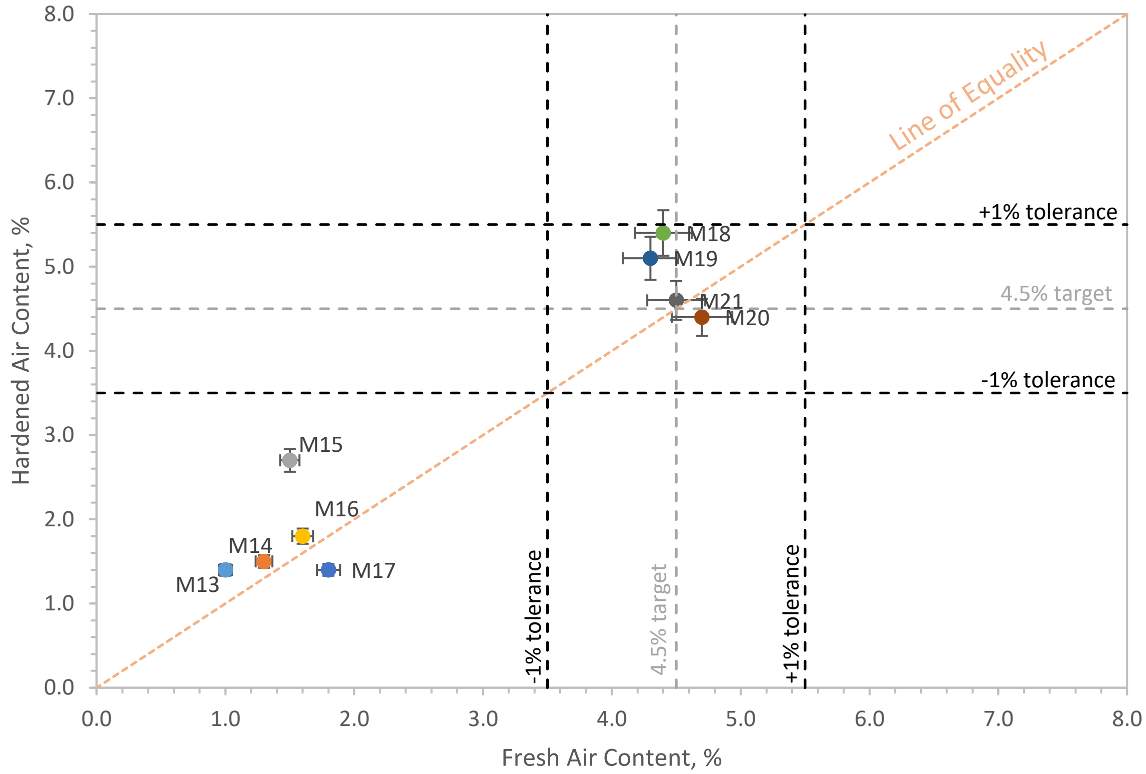


Figure 4.2 Comparison of air content measured in the fresh and hardened concrete for CEM II/B-V concretes with a line of equality

Table 4.2 Air void parameters for CEM II/B-V determined using the automated air void analyser

Mix Code	Air Content (Fresh), %	Air Content (Hardened), %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	[1)]Micro Air Content, %
Non-Air Entrained							
M13	1.0	1.4	0.073	98.50	0.347	0.041	1.1
M14	1.3	1.5	0.074	100.29	0.364	0.041	1.1
M15	1.5	2.7	0.082	74.28	0.499	0.054	1.8
M16	1.6	1.8	0.065	112.72	0.505	0.036	1.1
M17	1.8	1.4	0.095	90.14	0.303	0.045	0.9
Air Entrained							
M18	4.4	5.4	0.058	64.54	0.858	0.062	4.0
M19	4.3	5.1	0.058	72.32	0.909	0.056	4.2
M20	4.7	4.4	0.075	67.03	0.740	0.061	3.2
M21	4.5	4.6	0.068	73.48	0.842	0.055	3.2

1) Microair content is the total air content for void sizes <300μm in diameter

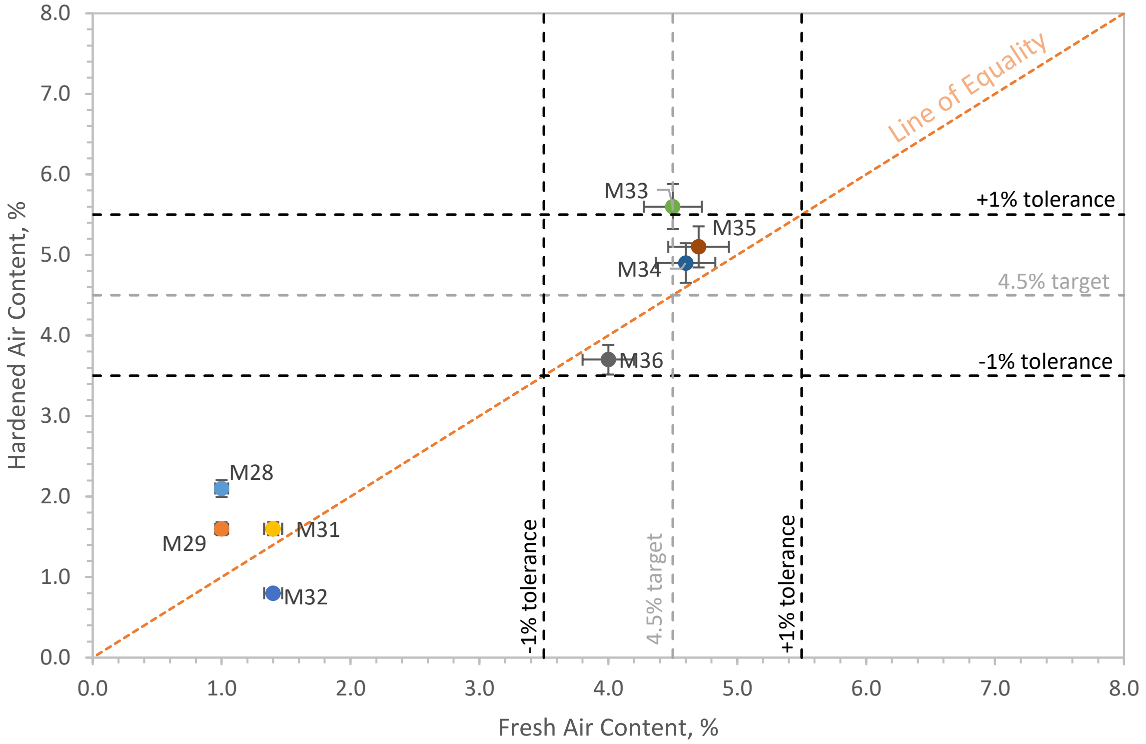


Figure 4.3 Comparison of air content measured in the fresh and hardened concrete for CEM III/A concretes with a line of equality

Table 4.3 Air void parameters for CEM III/A determined using the automated air void analyser

Mix Code	Air Content (Fresh), %	Air Content (Hardened), %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	[1]Micro Air Content, %
Non-Air Entrained							
M28	1.0	2.1	0.072	88.41	0.460	0.047	1.6
M29	1.0	1.6	0.104	72.09	0.280	0.056	1.0
M30	1.4	1.6	0.077	97.97	0.390	0.042	1.1
M31	1.4	1.6	0.083	100.34	0.370	0.044	1.1
M32	1.4	0.8	0.104	122.28	0.243	0.041	0.3
Air Entrained							
M33	4.5	5.6	0.057	62.57	0.882	0.066	3.9
M34	4.6	4.9	0.094	47.81	0.581	0.084	3.2
M35	4.7	5.1	0.067	68.59	0.876	0.059	3.8
M36	4.0	3.7	0.093	59.99	0.552	0.068	2.9

1) Microair content is the total air content for void sizes <300µm in diameter

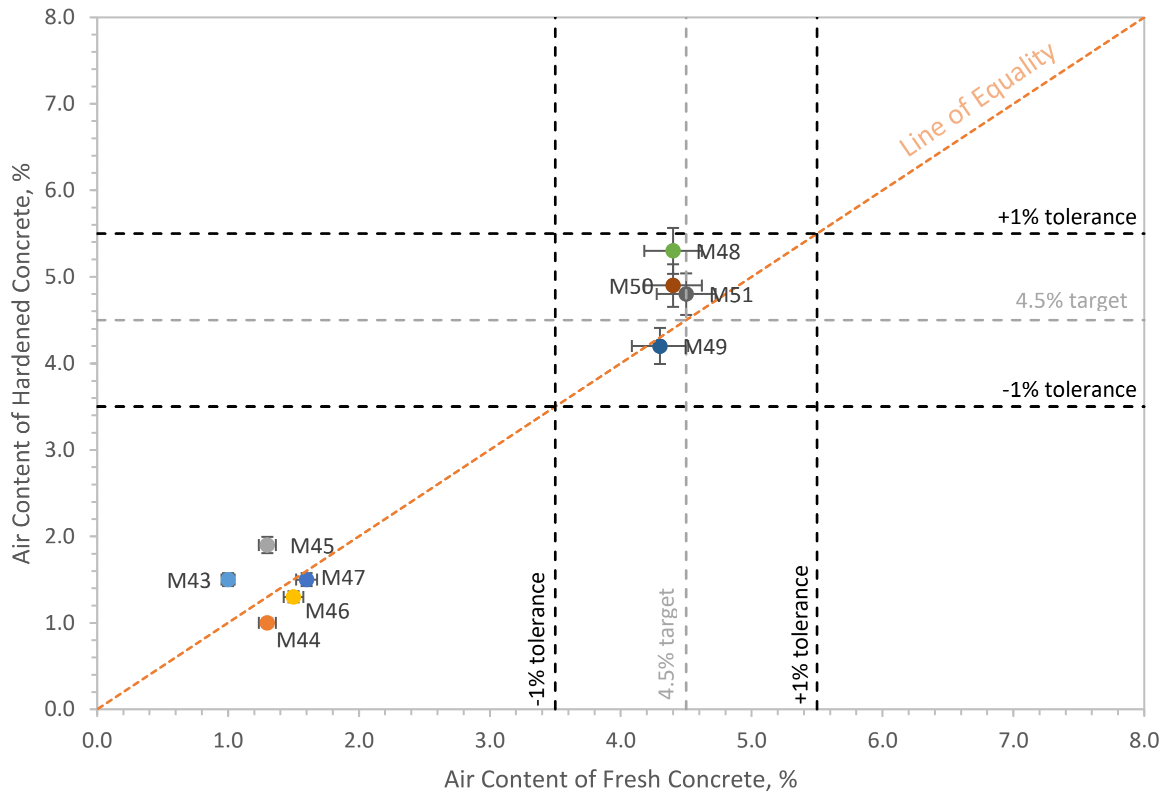


Figure 4.4 Comparison of air content measured in the fresh and hardened concrete for CEM II/A-L concretes with a line of equality

Table 4.4 Air void parameters for CEM II/A-L determined using the automated air void analyser

Mix Code	Air Content (Fresh), %	Air Content (Hardened), %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	1)Micro Air Content, %
Non-Air Entrained							
M43	1.0	1.5	0.097	73.53	0.286	0.055	1.1
M44	1.3	1.0	0.067	140.23	0.350	0.029	0.6
M45	1.3	1.9	0.088	79.76	0.378	0.051	1.4
M46	1.5	1.3	0.156	54.43	0.175	0.074	0.5
M47	1.6	1.5	0.078	107.35	0.392	0.038	0.6
Air Entrained							
M48	4.4	5.3	0.072	55.03	0.713	0.073	3.2
M49	4.3	4.2	0.050	99.51	1.070	0.041	2.9
M50	4.4	4.9	0.078	60.88	0.745	0.066	3.3
M51	4.5	4.8	0.077	64.49	0.757	0.063	3.2

1) Microair content is the total air content for void sizes <300µm in diameter

4.2.1.1 Spacing Factor

In Chapter 2, it was highlighted that for a long time Powers Spacing Factor characteristic became the value to determine the freeze-thaw resistance of concrete, enabling concretes to be selected before they were subjected to freeze-thaw testing. As superplasticizers and air entrainers have developed, the reliance on this parameter has become less dependable due to its fluctuating results particularly between non-air and air entrained concretes. As the results show in Table 1–4, non-air and air entrained illustrate to have similar results across the cement types. Powers (1945) defined the limit for an a freeze-thaw resistance concrete to be 250μm, but as the results shown most of the concretes are 100μm or below which Powers (1945) defined to be the optimum Spacing Factor values which suggests that these concretes will be able to provide an *Acceptable* scaling rating in accordance with SS 137344.

From the results and the continual development of admixtures the spacing factor characteristic should be updated to incorporate these developments and reduce the maximum spacing values. When analysed closely, the data shows a similar trend comparing the non-air and air entrained samples. 0.07 mm is seen to be the value where a concrete could be considered to have good freeze-thaw resistance. This would redefine the characteristic parameters set out by Powers for the Spacing Factor incorporating modern admixtures. However, using this definition would cause issues as many of the sample overlap this defining value, for example, M3 (non-air entrained) has a value of 0.068 mm and M7 (air entrained) has a value of 0.084 mm so the statement earlier cannot be introduced as there are other samples like this.

Reviewing the Spacing Factor in terms of the cement type, CEM I has no defining split between the non-air and air entrained concretes. The data shows the Spacing Factor for the concrete strengths do not provide a clear separation of the data for the air entrained concretes so using the parameter would not provide a comparison for the results. CEM II/B-V shows to have a slightly clearer comparison between the air and non-air entrained samples but it is difficult to distinguish between the values. Regarding the strength the Spacing Factor is unaffected as the strength increases but the parameter fluctuates between 0.065-0.095 mm for non-air entrained and 0.058-0.075 mm for the air entrained.

Non-air entrained CEM III/A concretes do show a degree of defining between the concretes with M29 and M32 showing higher values (0.104 mm for both). Other values lie within the same range as the air entrained concretes and defining these as to whether they can provide *Acceptable* scaling resistance would be hard to determine. M46 (50 MPa CEM II/A-L) has a value of 0.156 mm, higher than the others but would be deemed to be an outlier as the other non-air entrained concretes are within the range of 0.067-0.097 mm

The results for the Spacing Factor dictate there is a difficulty in defining a suitable concrete range given the results in the tables above. Unlike Powers (1945) who determined the limit of 250 μm to be the point where freeze-thaw resistance would be classified, concretes used with ever developing admixtures require a more up-to-date parameter to meet the developing admixtures. It can be concluded that the use of the Spacing Factor is not applicable at the very least by itself and would require one or two more parameters used in conjunction to define a concrete's acceptability for freeze-thaw resistance.

4.2.1.2 Specific Surface

Specific Surface is based upon the total surface area of the voids divided by volume to create a ratio of area to volume and the more voids that are present, the higher the value of the specific surface as the surface area increases more quickly than volume increasing the division of area over volume. Similarly, to the Spacing Factor parameter, the Specific Surface has a scatter of results regarding the non-air entrained concretes when compared individually. Reviewing the air void characteristic tables, it is shown that the non-air entrained samples are very scattered ranging from 54.43-140.23 mm^{-1} (for non-air entrained CEM II/A-L) which could be the result of the entrapped air affecting the results.

Whereas the results for the air entrained concretes are more closely grouped together with an outlier present. This suggests that with more voids present during the analysis there is an even spread of void sizes, albeit different sizes between 0-500 μm and more voids within the range compared to the non-air entrained concrete. Based on this assumption, it can be assumed that from the tables above other concretes of different strength and cement type will produce possible grouping of results depicting a trend where grouping around an approximate value could be considered the value for freeze-thaw resistance. Table 4.5 shows the comparison of non-air and air entrained concretes for the different cement types. This value will change depending on the cement type between the particle size distribution and the entrainment bubble sizes produced.

Table 4.5 Comparison between the grouping of Specific Surface results for the non-air and air entrained concretes for the respective cement type

Cement Type	**Non-air Entrained, mm^{-1}**	**Air Entrained, mm^{-1}**
CEM I	74.84 - 122.37	55.66 - 93.93
CEM II/B-V	74.28 - 112.72	64.64 - 73.48
CEM III/A	72.09 - 122.28	47.81 - 62.57
CEM II/A-L	54.43 - 140.23	55.03 - 99.51

Given the scatter of the results for the specific surface, it can be concluded there is no correlation between the parameter and the scaling loss. This would suggest that this parameter is not suitable to determine the freeze-thaw resistance of concrete. Comparing the specific surface to the spacing factor (Figure 4.5), it can be argued that there may be a correlation in the data, albeit, only CEM II/A-L where there is a matching spread in the data when the non-air and air entrained concretes are plotted. This allows for a direct comparison between the parameters but only if one parameter is not used to calculate the other.

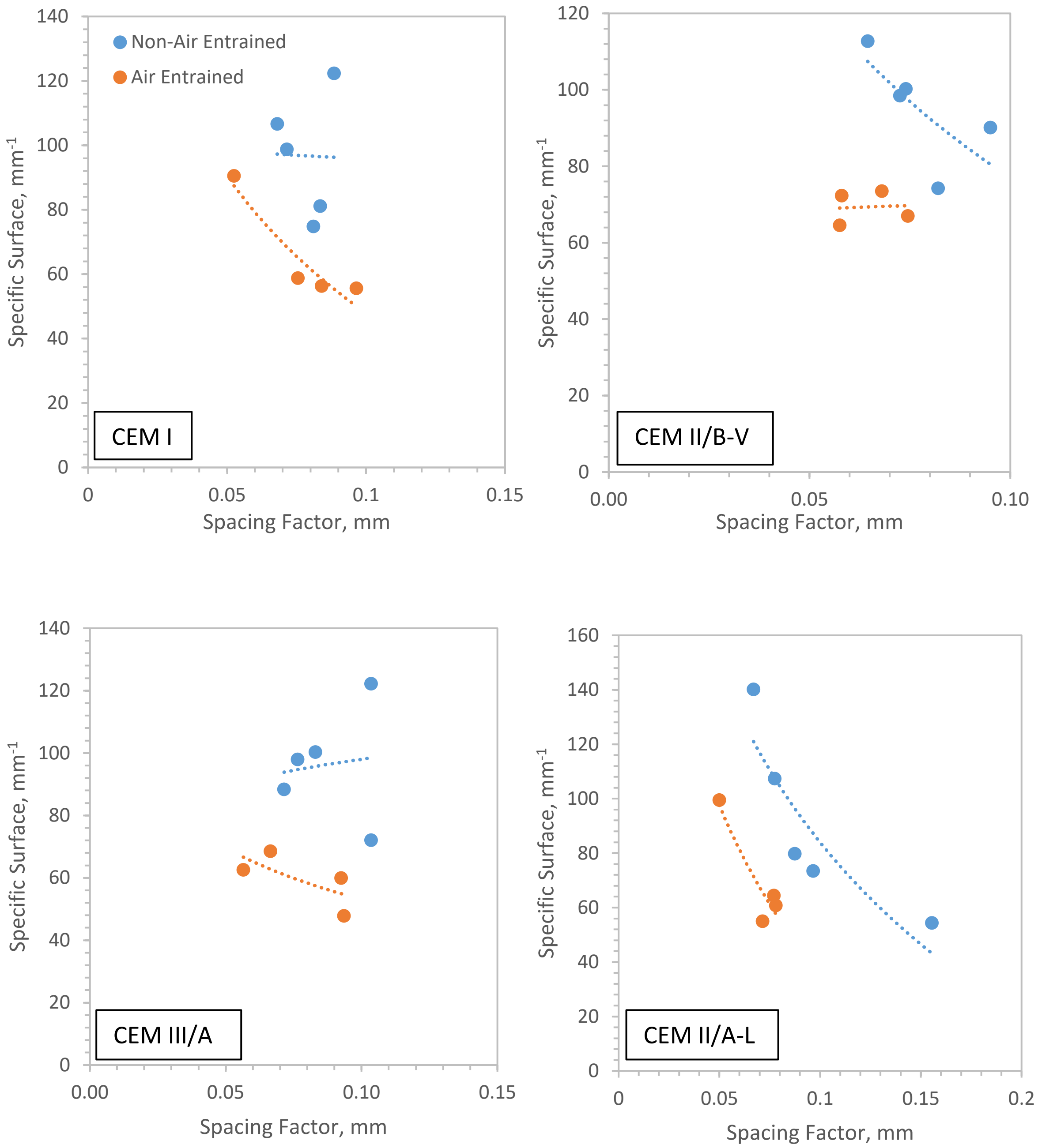


Figure 4.5 Comparison between the specific surface and spacing factor for the non-air and air entrained CEM I, CEM II/B-V, CEM III/A and CEM II/A-L concretes

4.2.1.3 Void Frequency

Void frequency provides a representation of whether concretes have an *Acceptable* freeze-thaw scaling resistance. From the results in the above tables, the difference between entrapped and entrained can be distinguished. As shown, most of the results are defined by being below 0.55 mm^{-1} for a non-air entrained concrete and above for air entrained. When comparing the results against the cement types there is a notable grouping of the results as shown in Table 4.6.

Table 4.6 Comparison between groups of void frequency between different cement types

Cement Type	Non-air Entrained, mm^{-1}	Air Entrained, mm^{-1}
CEM I	0.350 – 0.560	0.550 – 0.670*
CEM II/B-V	0.300 – 0.510	0.740 – 0.910
CEM III/A	0.240 – 0.460	0.550 – 0.890
CEM II/A-L	0.170 – 0.400	0.710 – 0.760*

*Range does not include outlier in each group

Determining a link with other parameters is more difficult as results are scattered. For example, when the void frequency is compared with the spacing factor there is a trend whereby higher the frequency, the lower the spacing factor for the air entrained samples, whereas the non-air entrained samples which have the same spacing factor (for different compressive strengths) shows different void frequency results making comparisons and correlations problematic. The only correlation with this parameter is with the air content in the hardened state but since this parameter is used to calculate the void frequency then the comparison would not be suitable.

Similarly to the specific surface, the void frequency was compared to the spacing factor to determine if there are any correlation in the data.

4.2.1.4 Average Chord Length

The Average Chord length is unsuitable in determining a concrete's freeze-thaw resistance for the simple fact that it is based upon the total number of voids counted and their respective diameters. Similar to the Spacing Factor, the Average Chord Length is an average of the total diameters counted providing a single value which represents the chord length for the entire sample. As stated, this an average and whilst it is quick and easy to ascertain a single representative length it will not be accurate enough. The parameter could be developed to aid in freeze-thaw examination of samples but from the results in Tables 1–4 it is arduous in refining what that point could be.

Simultaneously, the results do show a lower value for the non-air entrained concretes which can be construed as not being an acceptable concrete as the chord length is too small for water to fill the void rendering the void obsolete. Whereas air entrained concretes have a higher value meaning that AEA has managed to get inside the void and prevent it from collapsing providing voids for freeze-thaw resistance.

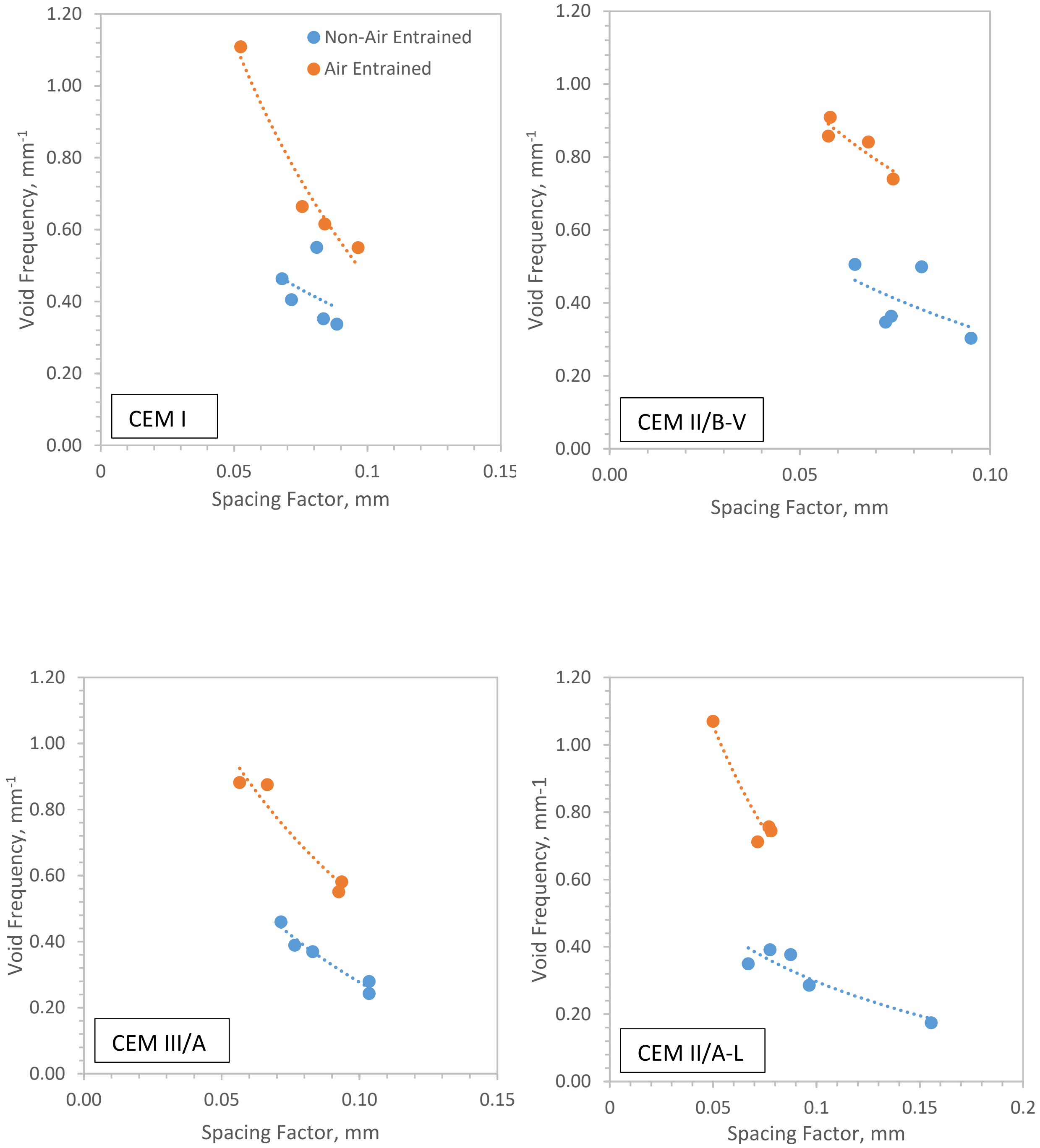


Figure 4.6 Comparison between void frequency and spacing factor for CEM I, CEM II/B-V, CEM III/A and CEM II/A-L non air and air entrained concretes

4.2.1.5 Microair Content

Unlike the other parameters, the microair content is only applicable to concrete samples tested in accordance with BS EN 480-11. It is defined as the total air content for all the voids less than 300 µm in diameter and it can be assumed that the standard defines this as the optimum air content. Microair content is a new parameter providing a basis and possibly the initial assessment of a concretes freeze-thaw resistance though this is open to interpretation as Eilsen (1994) provided different views on what could be classed as optimum air content.

BS EN 480-11 defines this parameter but there is no explanation as to why it has been used for or what the purpose is of the parameter. BS 8500 only defines the air content requirement for concrete not the microair content, so it is assumed the value is used to simply provide a value below a maximum diameter. It is then considered that with the consideration of an optimum air content there should be an optimum void size range.

The data in the tables above outline the microair content for different cement types and by comparing the microair content to the total air content it is approximately 66% of microair to total air content. This value is similar for all the cement types with some differences above and below. The microair content differ based on the cement types where microair contents for the air entrained CEM I and CEM II/A-L concretes group around the 3% microair content compared to 3.6% for CEM II/B-V and CEM III/A concretes.

As mentioned Eilsen (1994) highlighted that voids less than 50 µm do not have the ability to provide resistance as these spaces are not large enough to allow water, and ice, to move through. On top of the microair content there should have the parameter of optimum air content where the total air content between 50 µm to 500 µm would be the size range that determines the protective capacity of the concrete with a minimum value for, example 3.5%, with the total air content greater than 500 µm chord size adding to the resistance.

4.2.2 Higher Values of Air Content for Hardened Concrete Compared to the Fresh

During the analysis it was identified that the air content for the hardened concrete was higher than the fresh for most of the concretes. When the air content test is undertaken, the system is designed to force air into the chamber filled with compacted concrete and the amount of displacement determines the air content in the concrete. While the test does provide a good approximation, it is difficult to repeat the same test on the same concrete and still produce the same value with a repeatability and reproducibility values of 0.4% and 1.3% respectively (Table in Chapter 3 of standards). Moreover, there is no guarantee that the concrete at the bottom of the chamber will feel the effects of the air being forced into the chamber suggesting there is a possibility that only 75% (for example) of the concrete is being compressed. It could be argued that the remaining 25% at the bottom is compacted enough removing the entrapped air however, this would be difficult to prove.

Automated analysis proposes issues on the other side whereby the analysis conducted can be construed as too sensitive resulting in data being higher than it actually is. Hasholt (2014) had identified when different laboratories tested the same samples (in a round robin), different results were produced, with values up to nearly double in some cases. These differences relate to the preparations and settings of the equipment as white powder is used to create a contrast of the voids on the blackened concrete allowing for easier identification by the air void analyser, ultimately leading to an increase in the air content compared to the fresh air content.

As shown, the majority of the air contents for both the fresh and hardened concretes lie along the boundary of the line of equality which is the point where all the points would sit if the air contents of the fresh and hardened concretes were the same. The non-air entrained concretes (Series 1) tend to cluster around 1.4% air content. This would be from the resultant entrapped air (Wong, et al., 2011) but this is not the case as a small percentage would be from the entrained air produced by the superplasticizer. Air entrained concretes are grouped around the 4.4% value which is close to the target 4.5% outlined in BS 8500. Though the standard dictates that for XF concretes with a maximum aggregate size of 40mm to have a minimum air content of 4.0%, ((BSi, 2015a) states that there can be tolerance of ±1%.

When comparing the total paste contents for all the cement types (Table 4.7), the difference in the values is negligible however, the final results shown in Figure 4.7 depict a difference regarding the non-air entrained air content for each resultant compressive strength. Though it was observed that a reduction in the w/c ratio the strength of the concrete will increase, and this increase can also be seen in the air content. This would suggest that the increase in the air content would be in direct proportion to the increase in the air entraining admixture (or in this case the superplasticizer). Although considering that for most of the superplasticizer content stays mostly equal for other cement types (there are several which have a higher dosage), it can be contemplated that it is the entrapped air making the difference in the air content results. With the increase in the cement content, the viscosity of the mix would be keeping the air trapped within but the slumps for all the concretes cast remained in the S3 Slump Class (100-150 mm). Be that as it may, the increase in the cement content would increase the density of the concrete making the concrete more viscous trapping the air bubble within the concrete.

Table 4.7 Comparison between the non-air entrained target strengths and the total paste content for each cement type including cement, water and fine aggregate up to 1.18 mm

Target Strength, MPa	Total Paste Content, %			
	CEM I	CEM II/B-V	CEM III/A	CEM II/A-L
20	40.2	39.7	40.1	40.2
30	41.2	40.6	41.1	41.2
40	42.3	41.8	42.2	42.3
50	43.6	43.0	43.4	43.6
60	44.8	44.3	44.6	44.8

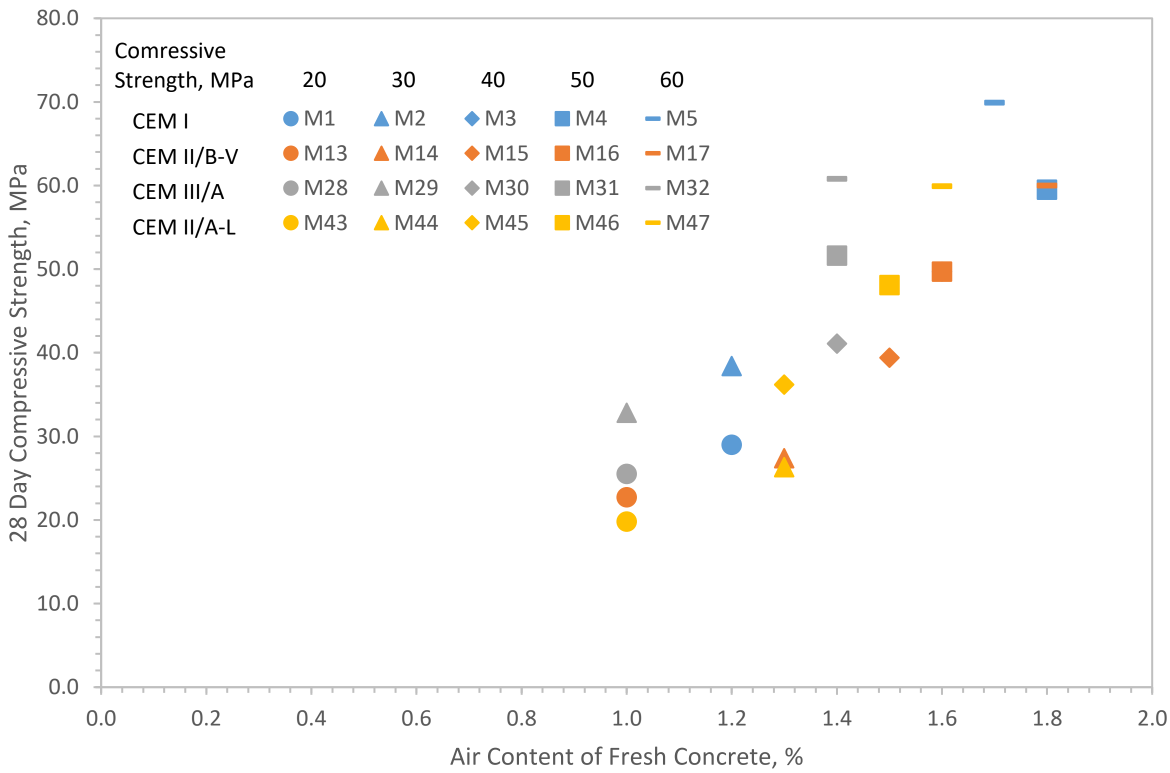


Figure 4.7 Comparison between the non-air entrained concretes of different cement types for the air content in the fresh state and the compressive strength at 28 days

4.2.3 Influence of Superplasticizer and Air Entraining Admixtures on the Spacing Factor

Although BS 8500 states that the air content has to meet minimum requirements, there are other parameters which determine how the concrete will behave during freeze-thaw attack. One characteristic which has been used almost exclusively for freeze-thaw is the spacing factor derived by Powers (1945) where suitable protection for freeze-thaw requires a spacing factor to be less than 250µm.

The spacing factor is the maximum distance in the cement paste from the periphery (boundary) of an air void to another (BS EN 480-11 and ASTM C 457). Ideally, the distance measured throughout the specimen would be the same when air entrainment is used. However, this is not the case, so the spacing factor is measured for all the voids then a final average is taken to give a result. The method is proved to provide an adequate measurement, thus, enabling suitable protection for the concrete. Figure 4.8 shows the influence of air content measured in the fresh and hardened concrete on the spacing factor. The air entrained concretes depict a trend where with the increase in the air content, the spacing factor decreases creating a direct relationship between the two parameters.

The fresh and hardened air contents have a similar grouping due to the same spacing factor used to compare the air content. The air entrained concretes for both states show to have close similarities regarding air contents remaining in the ±1% tolerance range showing that the concrete loses minimal air content despite being vibrated and compacted. This suggests that even though the concrete had a target slump class S3, being fairly workable, the concrete was able to retain the entrained air with a slight increase to replace that which is lost due to vibration and compaction.

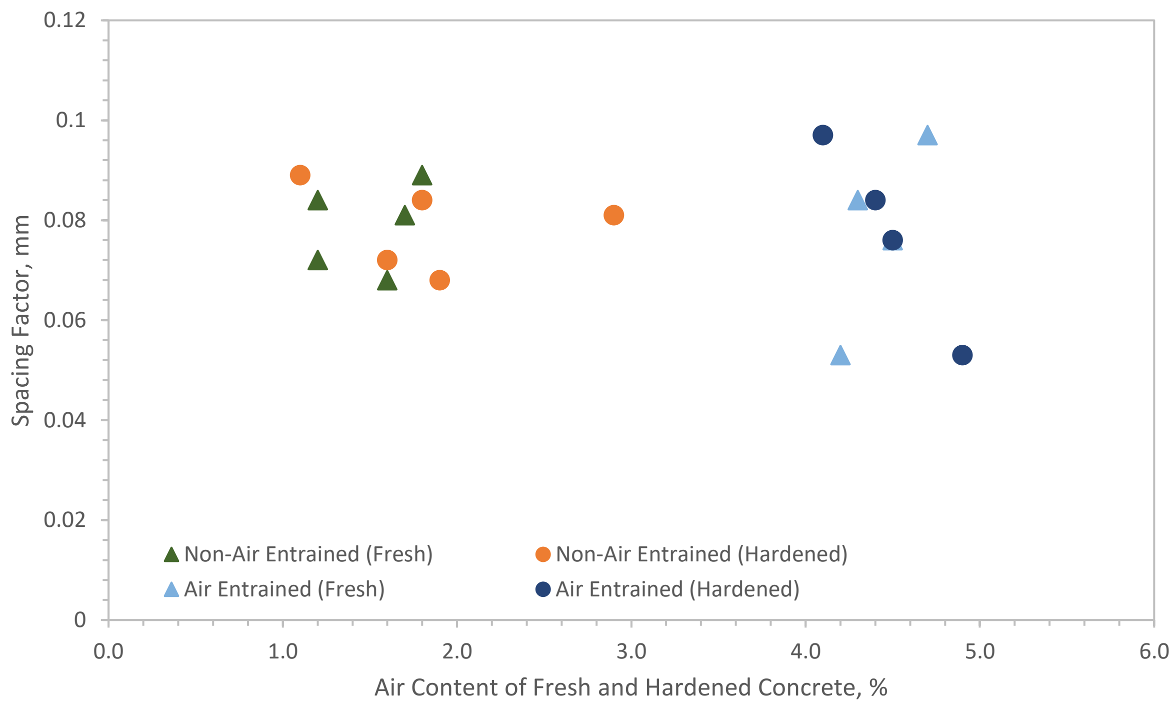


Figure 4.8 Air content of fresh and hardened concrete plotted against the spacing factor for CEM I concretes series 1 & 2 (M1-M9)

Furthermore from Figure 4.8, the spacing factors for the non-air entrained concretes have similar values to the air entrained concretes. In theory, with no air entrainment used only the entrapped air should be counted and the spacing factor value would be higher than 250µm as described by Powers (1945). For entrapped air voids, the Spacing Factor did not account for these in the calculation and consequently caused the value of the spacing factor to reduce. Another observation made was that the majority of the non-air entrained concretes in the fresh state show to have a slightly lower air content than the hardened concrete counterpart which is linked to the air content test. The test involves forcing air into the chamber of concrete and the percentage of displacement would be calculated air content and this was done instantly, although this involves compacting all the voids in the concrete there is no guarantee that voids at the bottom would be compacted to give the true value of the air content and would be difficult to determine with no previous data available. Whereas the air content of hardened concrete was conducted once 28 days of curing had occurred giving the concrete the time to solidify preventing the voids from moving during the test.

However, the spacing factor results shown in Table 4.1 for the non-air entrained concrete detail the spacing factors to be like that of the air entrained results. CEM II/B-V, CEM III/A and CEM II/A-L show similar results for the spacing factor (Table 4.2,Table 4.3 and Table 4.4 respectively). Focusing on the similarities, Figure 4.9 shows the total number of voids for each class size for both an air and non-air entrained concrete with the same strength (40 MPa).

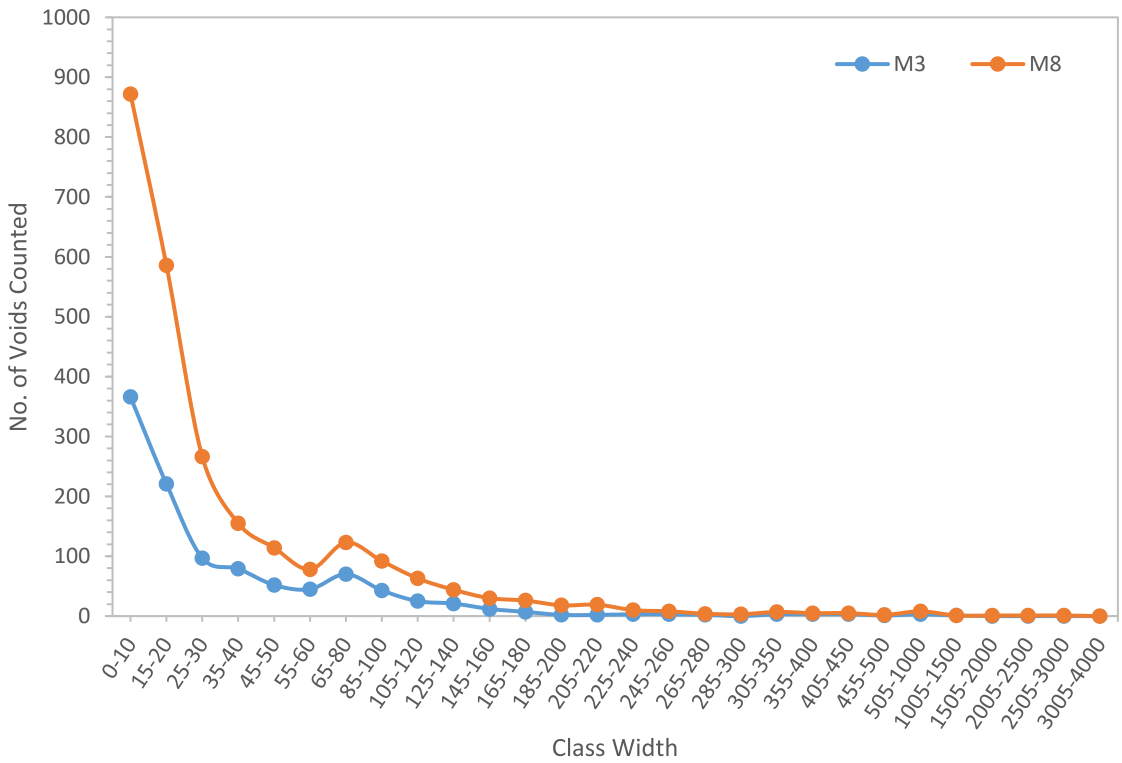


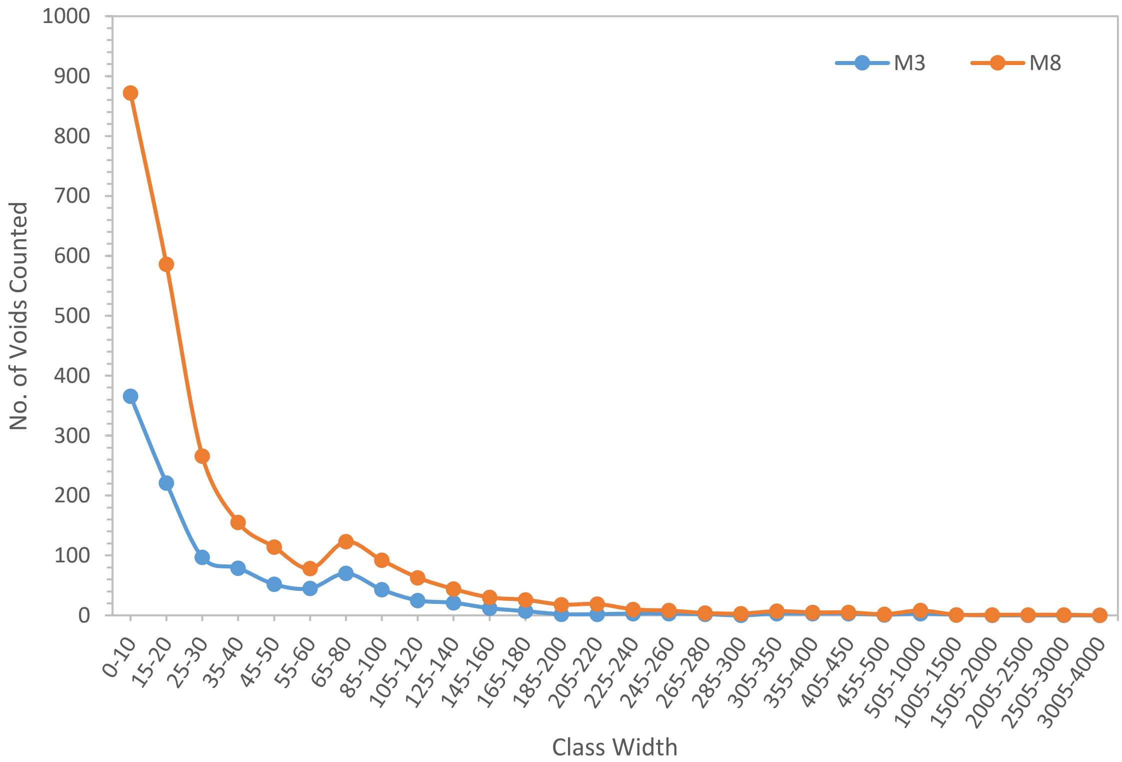
Figure 4.9 Comparison between 40 MPa CEM I non-air (M3) and air entrained concrete (M8) of the number of voids counted within a class width

The void sizes ranging from 0-30μm where most of the voids were counted, it is observed that a significant amount of voids were counted for M3, which is an non-air entrained concrete, leading the author to believe that the addition of a superplasticizer increases the number of voids counted due to having the side benefit of air entraining properties. Taking account of the air entrainment second function from the superplasticizer, the extra entrainment affects the results for the spacing factor for both air and non-air entrained concretes. As shown in the tables, the spacing factors are nearly the same as the air entrained samples as a result of the superplasticizer. Building on from that, a hypothesis was considered which details why the spacing factors are very close between the air and non-air entrained concretes:

'The inclusion of superplasticizer in a non-air entrained concrete affects the results of the spacing factor due to its secondary function of air entrainment. The possibility of validating a concrete's freeze-thaw performance based on the spacing factor is inert as no true value can be calculated with the continual development of superplasticizers.'

Normally, concretes which have a requirement to be air entrained use air entraining admixture to ascertain the target air content that produces a spacing factor. However, admixtures used today tend to have side benefits like superplasticizers which now has air entraining benefits adding to the total air content.

During the analysis it was investigated that the superplasticizer alone was influencing the spacing factor rather than the air content, but rather reducing the distance between voids slightly it seems to produce results identical to air entrained concrete. Considering



, the additional air entrainment from superplasticizer causes many small voids to form (<30μm) but not significantly adding to the air content. Instead the spacing factor is affected because of the higher number of smaller voids. Figure 4.10 illustrates how the spacing factor is affect by the increased number of voids.

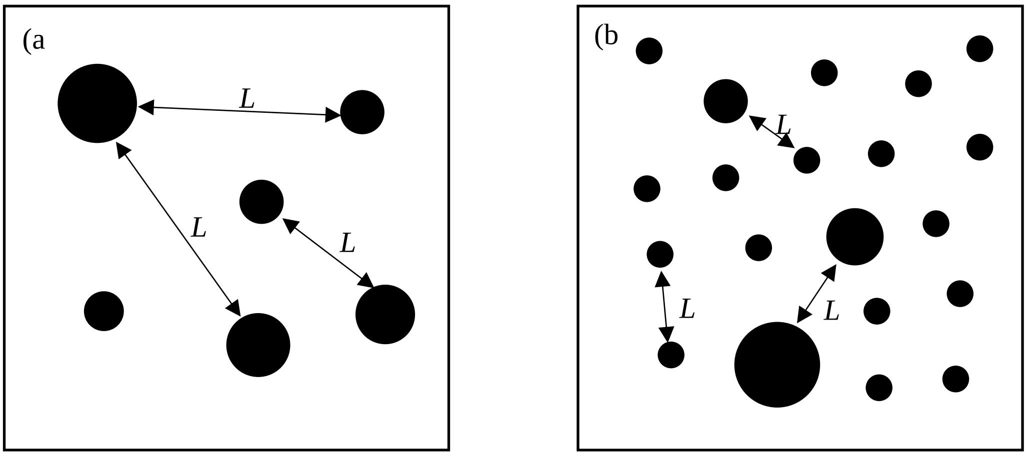


Figure 4.10 (a) spacing factor (*L*) measured of concrete with entrapped air, and (b) spacing factor (*L*) measured with superplasticizer only

Typically, when the air content is increased the spacing factor is reduced to account for the increased number of voids. So as more entrainment is used the distance between the voids decreases resulting in better protection against freeze-thaw. This means that using the spacing factor parameter to determine a concrete's ability to withstand freeze-thaw is much more difficult because to the different admixtures that are available with other benefits.

4.2.4 Using Specific Surface Air Void Parameter Rather than Spacing Factor

Since it was derived over 70 years ago, Powers spacing factor has been the main parameter which determines how well a concrete specimen would perform during freeze-thaw attack. This provided guidelines as to ensure enough entrainment was used. However, the development of new concretes and admixtures has caused the Spacing Factor to be challenged regarding its validity for use on modern concretes. In a paper produced by Hasholt (2014), the parameter was challenged as being accurate enough to base results off. It was found that using either specific surface or void frequency was better suited as these parameters could predict the likelihood that a capillary pore was connected to an air void whereas the spacing factor expressed the likelihood that the capillary pore was in the same area as an air void.

The specific surface parameter is the total surface area divided the volume of air that has been intersected by the traverse line. Looking at the tables above it has been identified that with air entrainment the specific surface decreases compared to the non-air entrained samples. Moreover, the value for the specific surface is given as a total area rather than an average like the spacing factor, so rather an average taken which may not be a good representation of the true values, it gives results which closely represent the true values calculated. Although BS EN 480-11 does not stipulate an error margin, a paper produced by Liu, et al. (2015) indicated that the maximum error margin for the spacing factor was ±9.1% for a 95% confidence interval.

Figure 4.11 and Figure 4.12 show the comparison between the specific surface and the measured air content of fresh concrete for non-air entrained and air entrained (Series 1 & 2) CEM I and CEM II/B-V concretes respectively. Using the specific surface parameter in conjunction with air content rather than spacing factor, Figure 4.11 illustrates there are groupings between the air and non-air entrained concretes with the air entrained samples showing a lower specific surface.

The correlation shows that with the increase in the air content the value for the specific surface decreases creating a direct correlation between the two parameters. In fact, it is quite the opposite in that the specific surface is determined from the distribution of air void sizes. Air entrainment is dependent on the foaming of the air entrainer during the mixing process and in doing so creates bubbles of all different sizes so it is beneficial to express the bubble size in terms of the specific surface which is another means to presenting the average bubble size as a unit length of measure (mm^{-1}). In other words, it is the cumulative measure of all the voids in the concrete represented as a single length as though the air content contained in the concrete was one single void.

From the figures, there is a correlation between the air content and the specific surface as expected regarding comparing the air and non-air entrained concretes. Specific surface is the measurement of area divided by the volume of the void and for a non-air entrained concrete the voids are large as it is assumed that most are entrapped air with some entrained air present from the use of a superplasticizer (SP). As the voids become smaller, through the use of air entrainment, the area of the void becomes larger than the volume creating a longer linear length for the specific surface, thus, with many of the smaller voids the average size will be smaller giving an overall larger length.

Increasing the air content reduces the specific surface due to an increase in the frequency of the voids. If the air content increased further, then the specific surface result would decrease. This statement, however, is not true as the total spacing factor is determinate on the average value across the void size distribution. Although most of the void sizes are in the range of 0-50μm, it will keep the average the same until a much larger void with a small specific surface reduces the total average specific surface. This means that the more voids in the concrete, the smaller the specific surface.

When compared to the spacing factor parameter the correlation between the results is far better for the specific surface giving 76% and 73% (Figure 4.11 and Figure 4.12 respectively). Similar results are seen with CEM III/A and CEM II/A-L concretes.

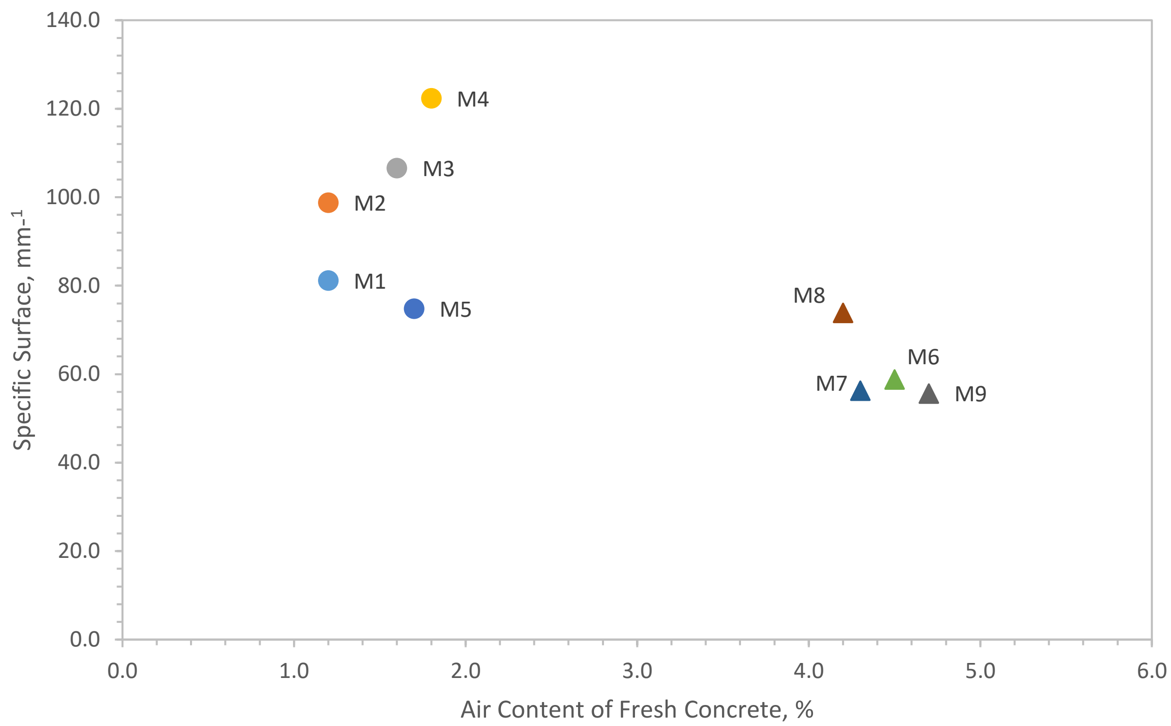


Figure 4.11 Comparison between the specific surface and the measured air content of fresh concrete for non-air entrained and air entrained (Series 1 & 2) CEM I concretes

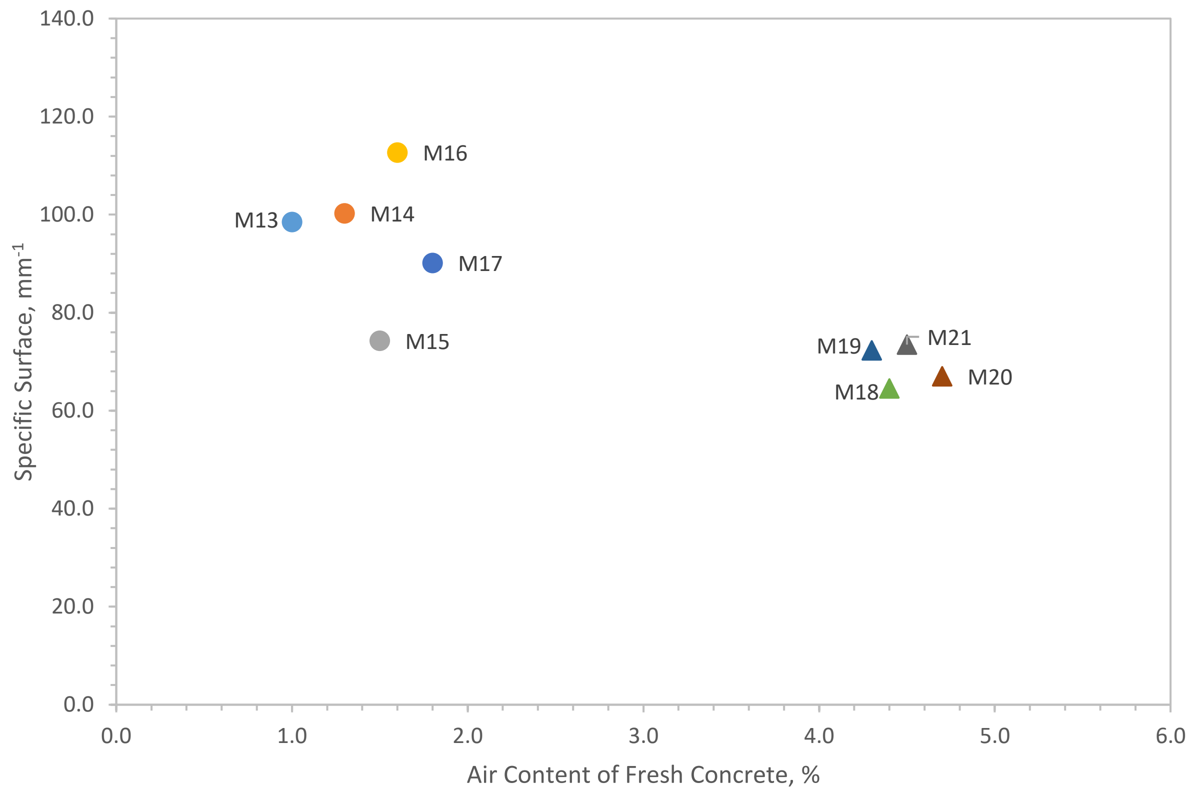


Figure 4.12 Comparison between the specific surface and the measured air content of fresh concrete for non-air entrained and air entrained (Series 1 & 2) CEM II/B-V concretes

4.2.5 Air Void Characteristics of Concrete with Varied Air Contents (Series 3)

BS 8500 outlines the minimum specification for the air content dependent on the maximum aggregate size for XF exposed concretes. Series 3 cast concretes with ranging air contents to determine the microstructural properties with such higher air contents. Figure 4.13 and Figure 4.14 show the air contents for the fresh and hardened states for the four different concrete types along with Table 4.8 and Table 4.9 showing the other parameters relating to the microstructure.

Figure 4.13 shows the air contents close to the line of equality apart from M12 which has a significant difference between the fresh and hardened air contents. CEM III/A and CEM II/A-L concretes have similar fresh and hardened air contents. Comparing the target air contents to the resultant contents, there are large discrepancies between the values. In order to reach the higher air contents, the air entrainment needs to increase exponentially reach the high air contents. However, whilst increasing the air entraining admixture content it was observed that after a certain point, the air content plateaued and the continual increase in the dosage only further increased the workability rather than the air content.

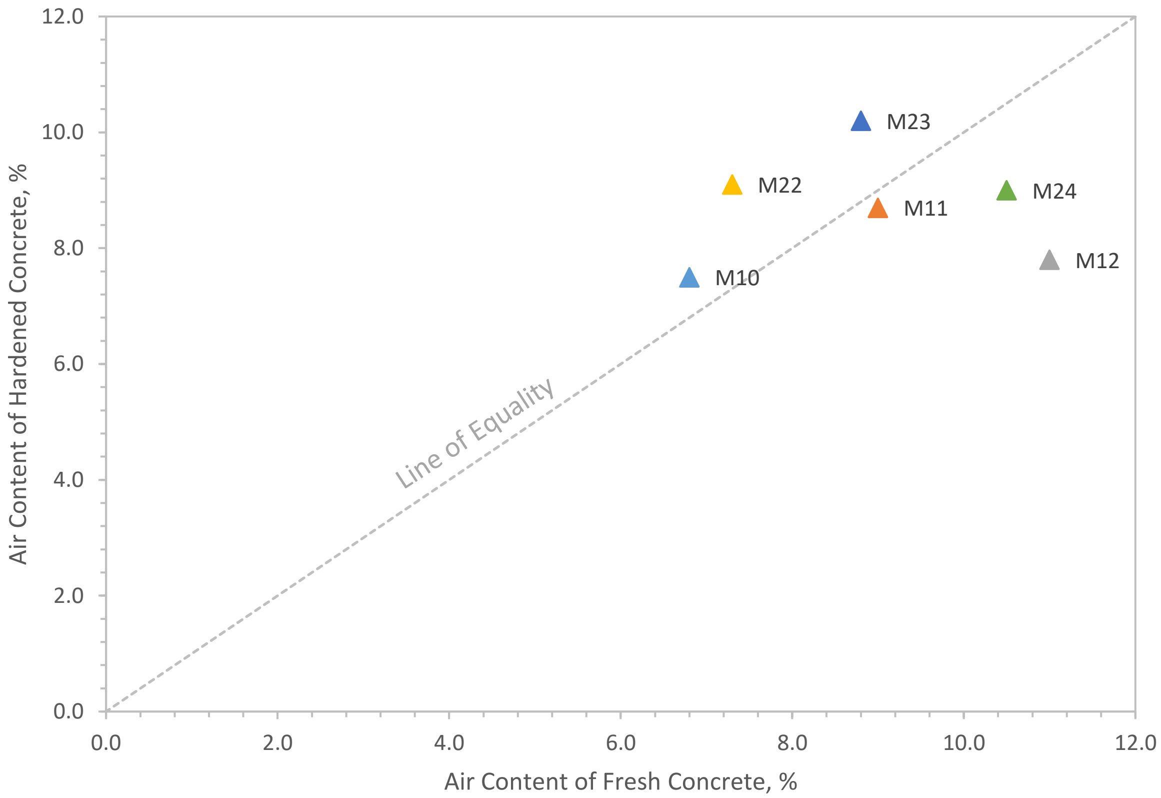


Figure 4.13 Fresh air content plotted against hardened air content for CEM I and CEM II/B-V with a line of equality for varied air content (Series 3)

Table 4.8 Air void parameters for CEM I and CEM II/B-V with varied air content (Series 3) determined using the automated air void analyser

Mix Code	Air Content (Target), %	Air Content (Fresh), %	Air Content (Hardened), %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
CEM I								
M10	7.0	6.8	7.5	0.042	87.78	1.675	0.046	5.5
M11	9.5	9.0	8.7	0.045	65.35	1.402	0.062	6.7
M12	12.0	11.0	7.8	0.043	74.52	1.446	0.054	5.9
CEM II/B-V								
M22	7.0	7.3	6.9	0.051	69.96	1.201	0.058	4.9
M23	9.5	8.8	10.2	0.033	76.87	1.963	0.052	7.2
M24	12.0	10.5	9.0	0.039	70.17	1.571	0.057	6.3

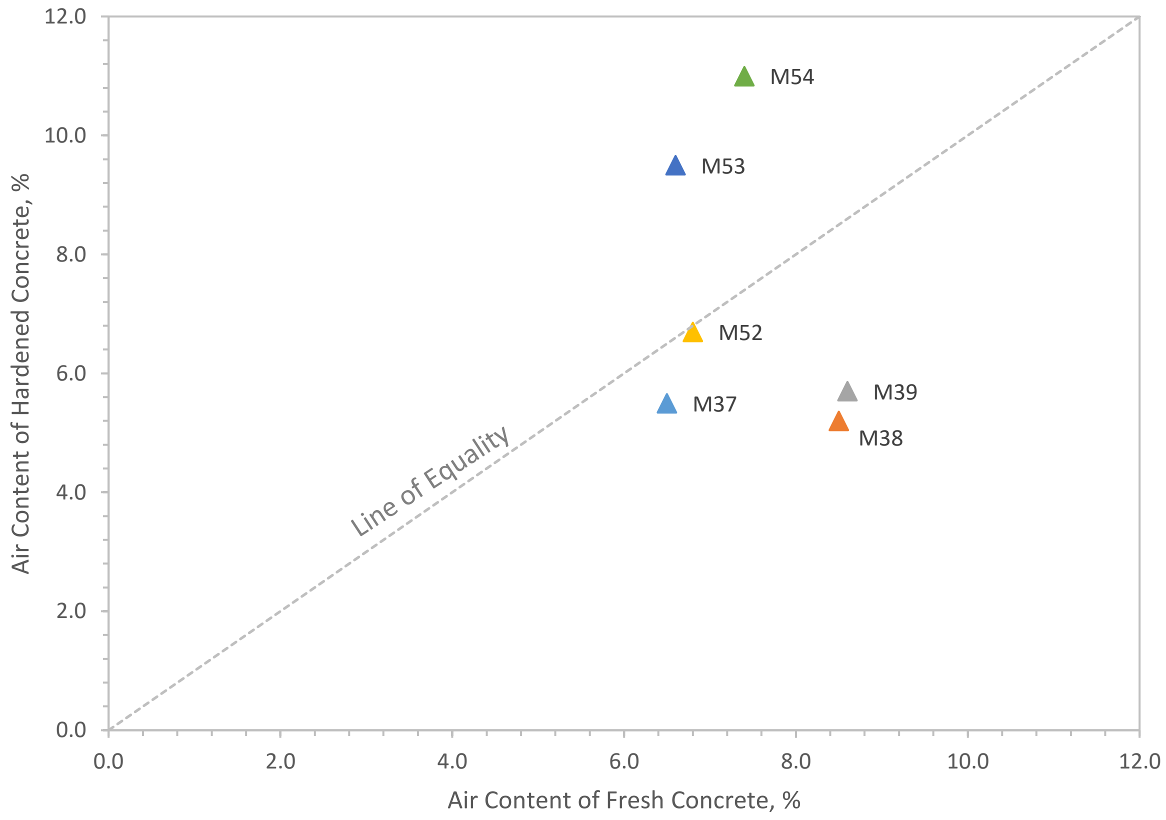


Figure 4.14 Fresh air content plotted against hardened air content for CEM III/A and CEM II/A-L varied air content (Series 3) with a line of equality

Table 4.9 Air void parameters for CEM III/A and CEM II/A-L with varied air content determined using the automated air void analyser

Mix Code	Target Air Content, %	Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
CEM III/A								
M37	7.0	6.5	5.5	0.045	97.66	1.334	0.041	3.5
M38	9.5	8.5	5.2	0.054	83.97	1.099	0.048	3.8
M39	12.0	8.6	5.7	0.045	94.99	1.357	0.043	4.1
CEM II/A-L								
M52	7.0	6.8	6.7	0.057	65.71	1.095	0.062	5.0
M53	9.5	6.6	9.5	0.045	62.23	1.45	0.065	7.1
M54	12.0	7.4	11.0	0.034	68.47	1.869	0.060	8.0

Increasing the dosage of air entraining admixture also affected the strength of the concrete but not in the way it was expected. It was assumed that without increase in the cement content the strength of the samples would decrease significantly, especially for the concrete using replacement materials. Out of all the samples, CEM I strengths were affected the most with a reduction of 5% on average with a 1% increase in the air content. CEM II/B-V saw a reduction of 1% in strength on average with a 1.8% increase in the air content and M22 improving on its strength completely compared to its standard air entrained counterpart (M20).

CEM III/A concretes were to poorest showing a decrease in compressive strength of approximately 10% for an increase in 1% air content. CEM II/A-L shown to have a reduction of 3% in strength for every 1% increase in the air content. These values show that when a non-standard increase in the air content is required then rather than using standard CEM I the better options would be to use either CEM II/B-V or CEM II/A-L as the loss in strength is lower than CEM I.

Although the dosage is consistently increasing to try and reach the target air content, the cement content has remained the same meaning the strength would decrease. Typically, when the air content increases the strength decreases because the cement content has not been altered to keep the target strength the same but also to accommodate the air entrainment. Figure 4.15 shows the comparison between the air content of the hardened concrete against the compressive strength.

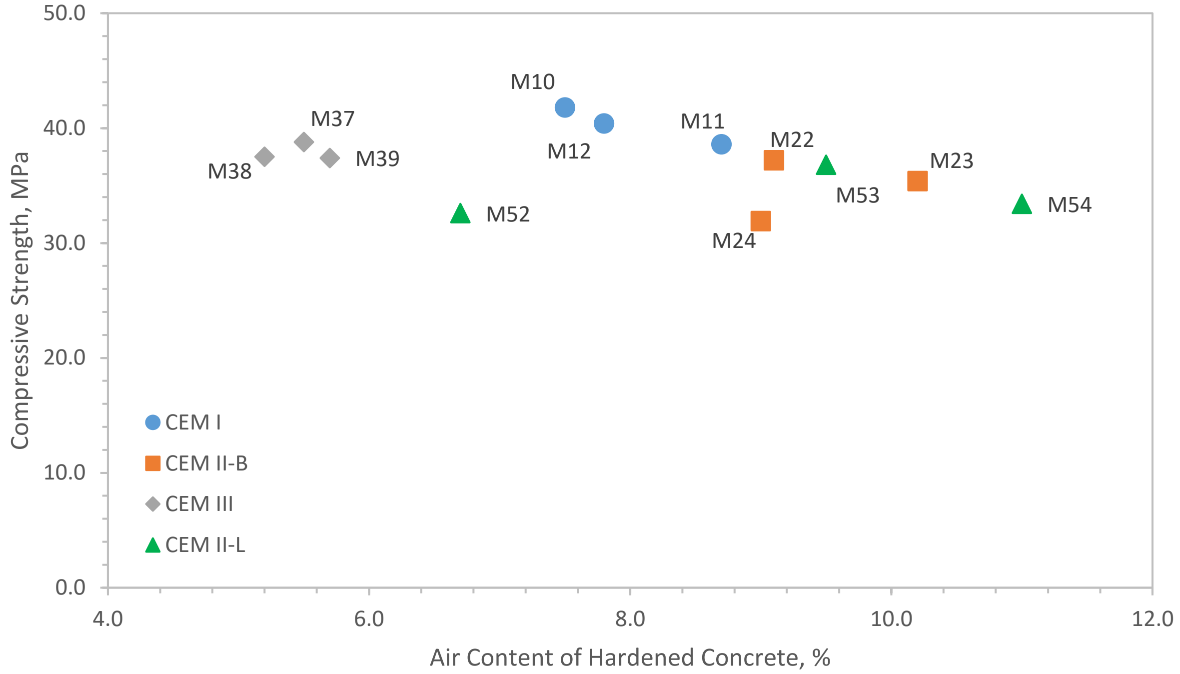


Figure 4.15 Air content of hardened concrete plotted against the compressive strength for CEM I, CEM II/B-V, CEM III/A and CEM II/A-L varied air contents (Series 3) concretes

The spread of the results on Figure 4.15 show different reactions to the increase in admixture. CEM I, CEM II/B-V and CEM III/A show the same grouping of the results as the strengths and air contents are approximately the same when increasing the dosage. Though CEM II/A-L shows a wider spread by comparison with the air contents of the hardened concrete ranging between 6% and 11%. Ordinarily, there would be a reduction in the strength with an increase in the air content but with CEM II/A-L the strengths remain relatively level. Although limestone addition is chemically inert, the particle size would affect the strength properties. Tsivilis, et al. (2002) showed that reducing the particle size of the cement/addition increases the strength of the concrete up to 10% limestone addition. Overall, the addition of a finer material can be a benefit to the compressive strength, but further addition content will effectively reduce a concrete's compressive strength.

4.2.6 Air Void Characteristics of Concretes with Different Replacement Content Percentages (Series 4)

Series 4 focuses on the microstructure of the concrete when the replacement percentages are increased whilst maintaining a constant target air content of 4.5%. Figure 4.16 illustrates the air content of the fresh and hardened concretes and Table 4.10 describes the parameters determined by the analysis. Each of the concretes were increased in 10% increments from the maximum allowance outlined in BS 8500 for freeze-thaw attack.

Series 3 concretes had a fixed design mix used in series 2 and then the air contents of the mixes were increased to determine the impact not only on the air void characteristics but the compressive strength too. Series 4 required a target strength and air content of 40 MPa and 4.5% respectively whilst increasing the replacement percentage.

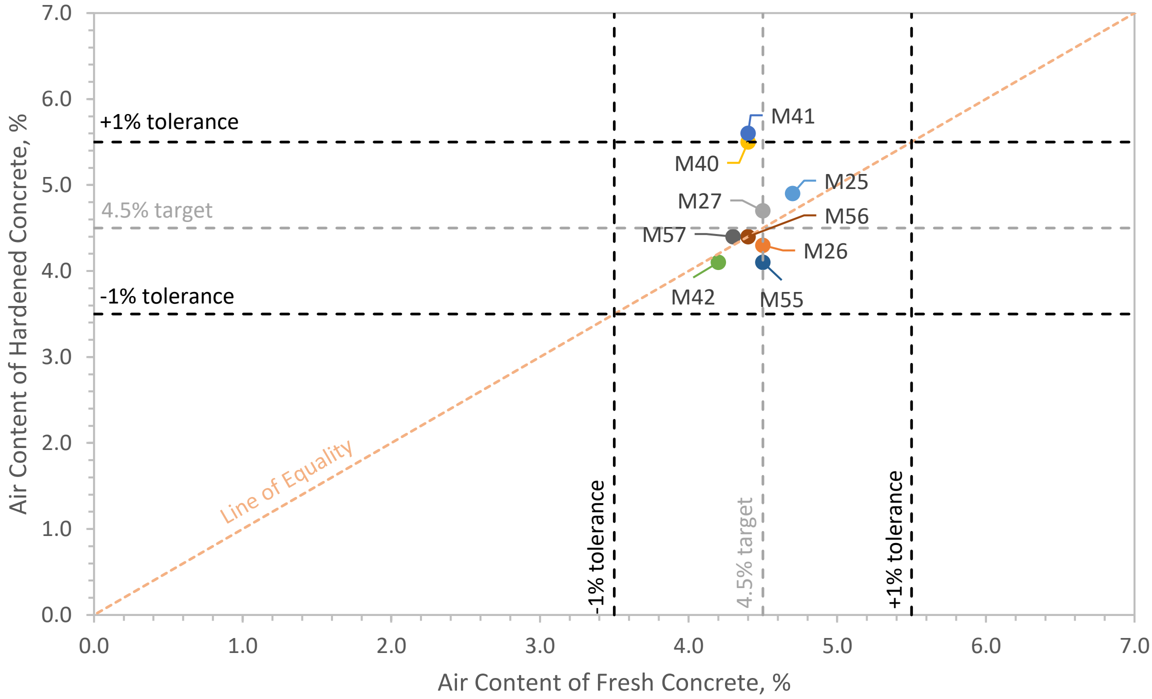


Figure 4.16 Fresh air content plotted against hardened air content for CEM II/B-V, CEM III/A and CEM II/A-L varied replacement content (Series 4) with a line of equality

Table 4.10 Air void parameters for CEM II/B-V, CEM III/A and CEM II/A-L with varied replacement content (Series 4) determined using the automated air void analyser

Mix Code	Replacement Content, %	Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
CEM II/B-V								
M25	45	4.7	4.9	0.078	69.96	0.721	0.069	3.6
M26	55	4.5	4.3	0.044	76.87	1.192	0.037	3.2
M27	65	4.5	4.7	0.050	70.17	1.001	0.046	2.2
CEM III/A								
M40	65	4.4	5.5	0.047	91.52	1.197	0.045	4.2
M41	75	4.4	5.6	0.040	110.7	1.543	0.036	4.2
M42	85	4.2	4.1	0.068	79.51	0.846	0.053	3.0
CEM II/A-L								
M55	30	4.5	4.1	0.041	121.92	1.255	0.033	3.1
M56	40	4.4	4.4	0.060	86.48	0.873	0.050	3.0
M57	50	4.3	4.4	0.054	97.27	1.114	0.044	3.4

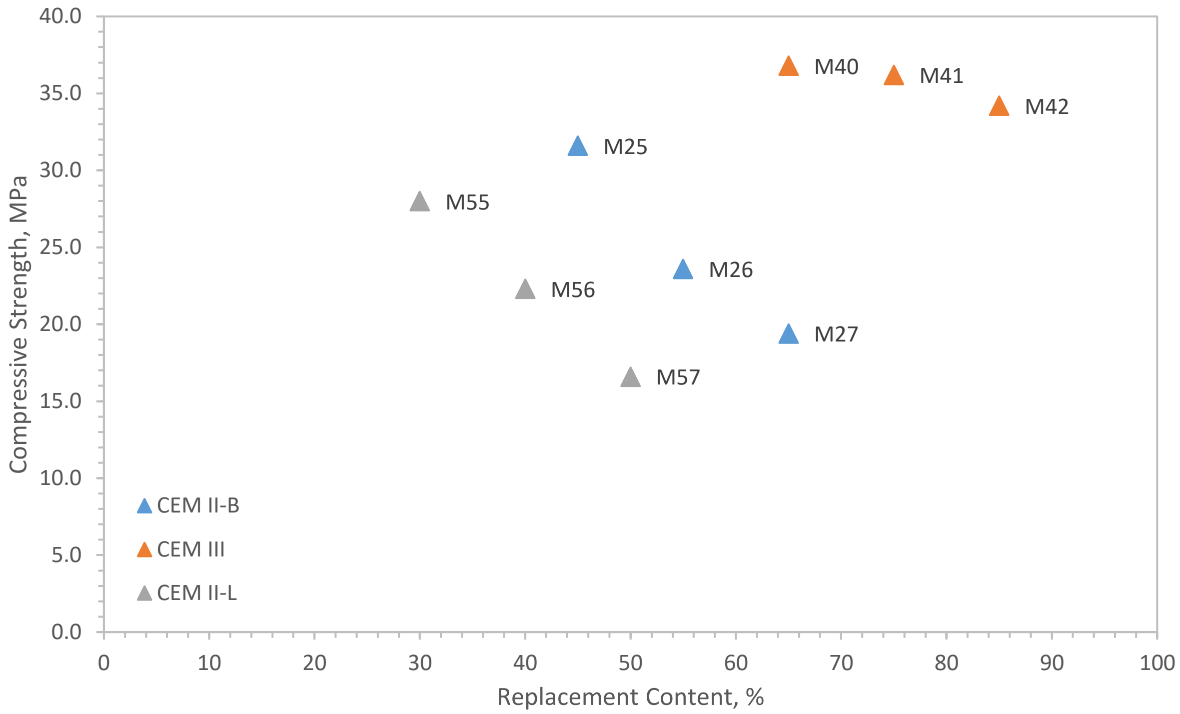


Figure 4.17 Compressive strength of different concrete types with different addition values above the limit stated in BS 197-1 and BS 8500 for freeze-thaw (Series 4)

Figure 4.17 shows how increasing the replacement content affects the compressive strength. As expected, the increase in the replacement material causes a decrease in the compressive strength. For CEM II/B-V and CEM II/A-L the average reduction for the compressive strength 22% for every 10% CEM I replaced. Contributing to the strength loss is the inclusion of air entraining admixture. In Series 2, the cement content was increased to accommodate the increased air content. However, in series 4 the cement and air contents were constant and only the replacement content was increased. Since CEM I was being reduced the compressive strength would reduce also.

CEM III/A saw a smaller strength loss of 3.5% for every 10% replaced for air entrained concrete. It has already been stated that using air entrainment in CEM III/A mixes does not aid in protecting the concrete during freeze-thaw attack even when the target air content has been reached. However, with a reduction in the total particle size distribution combined with the addition of air entraining admixture, the reaction could help retain the minimal strength loss as seen in Figure 4.17.

4.2.7 Air Void Characteristics of XF4 Non-Conforming Aggregate Concrete

In accordance BS 8500, concrete which is subjected to XF3 and XF4 exposure class are required to have aggregates which are capable to withstand freeze-thaw attack. The standard dictates that for these exposure classes, the aggregates must have a magnesium sulphate (MS) value of 25 and 18 for XF 3 and XF4 exposure classes respectively. This ensures that the total mass loss during freeze-thaw testing of the concrete is minimized from the aggregate. Typically, granite, which has an MS value less than 18, is used in situations where extreme freezing and thawing is taken place. This section looks at using the local aggregate so that analysis on the air void characteristics can be conducted to determine how well the material would perform when subjected to freeze-thaw.

Analysis was conducted on different concrete types to look at how the air void parameters differ compared to the granite.

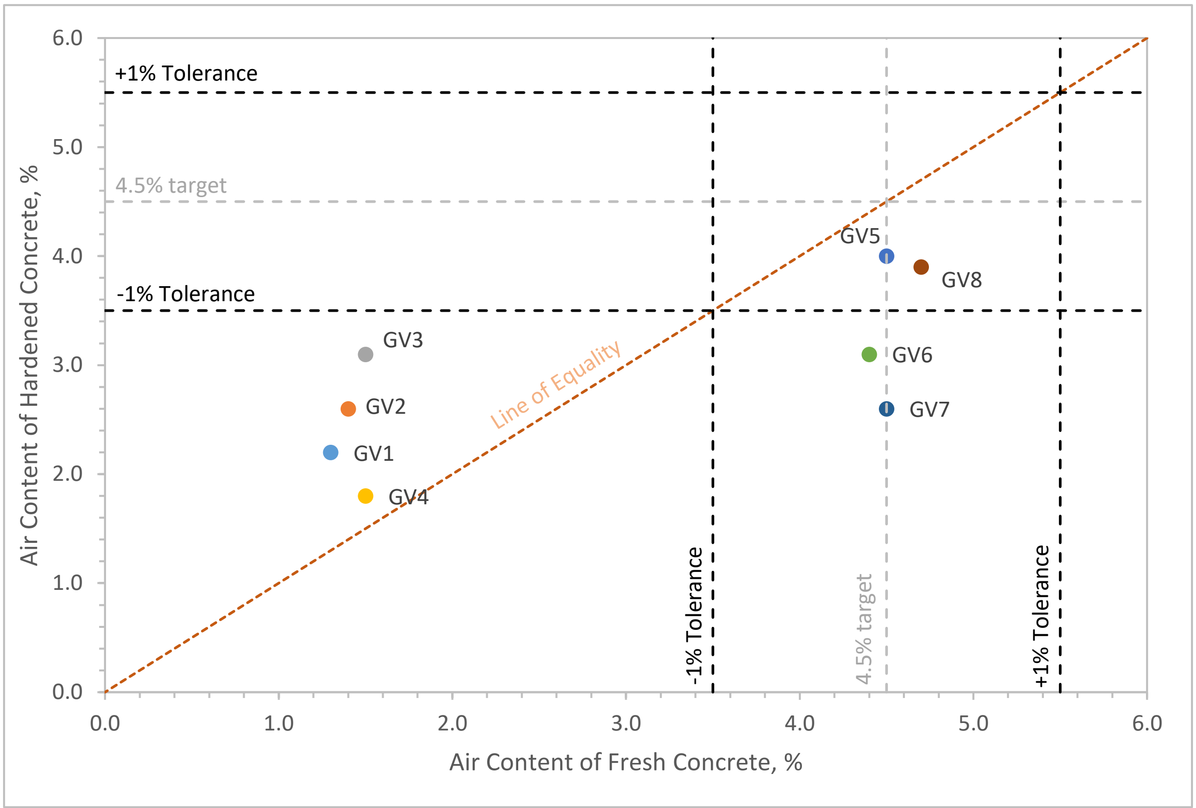


Figure 4.18 shows the air contents of the fresh and hardened concretes with Table 4.11 showing all the air void characteristics. Both the non-air and entrained concretes stay together in separate groups but more interestingly is that the non-air entrained samples have a higher air content in the hardened state whilst the air entrained samples have a higher air content in the fresh state. This is linked to the type of aggregate used.

The air entrained concrete containing gravel has an air content less than granite which can be attributed to the porosity of the gravel. Water may not be readily available during the mixing process and if it is the material would not be fully saturated when the air entrainer is added. If this is the case then the aggregate will absorb a portion of the admixture reducing the amount of admixture, therefore, reducing the total air content. Even though there is a reduction in the air entrainer the porosity of the gravel adds to the air content by, in a way, replacing the admixture lost. But this only replaces a minor amount, hence, a larger difference in the total air content.

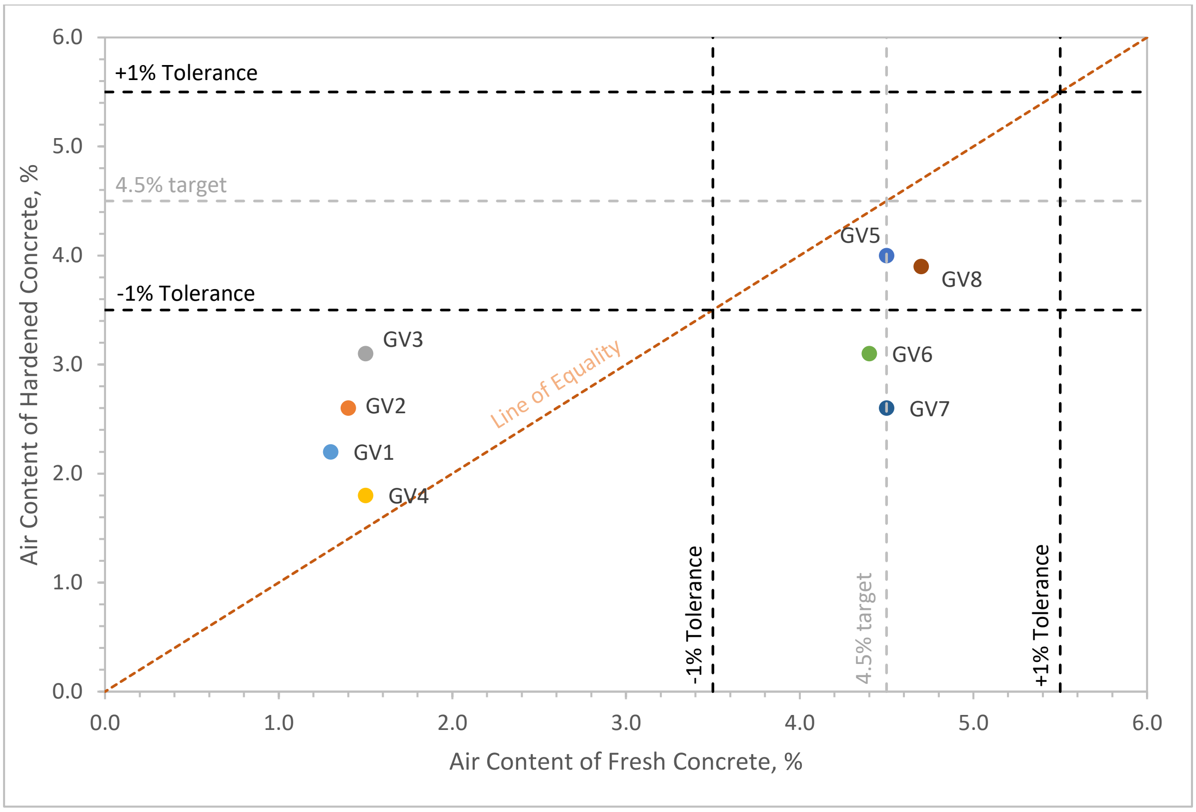


Figure 4.18 Air content of fresh concrete plotted against air content of hardened concrete for concrete containing gravel aggregates with a line of equality

Table 4.11 Air void parameters for concrete containing non-XF4 aggregates determined using the automated air void analyser

Mix Code	Concrete Type	Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
Non-Air Entrained								
GV1	CEM I	1.3	2.2	0.080	80.04	0.450	0.050	1.4
GV2	CEM II/B-V	1.4	2.6	0.062	96.34	0.362	0.042	1.7
GV3	CEM III/A	1.5	3.1	0.064	88.23	0.694	0.047	1.9
GV4	CEM II/A-L	1.5	1.8	0.100	70.88	0.326	0.057	1.2
Air Entrained								
GV5	CEM I	4.5	4.0	0.071	73.01	0.723	0.056	2.6
GV6	CEM II/B-V	4.4	3.1	0.067	87.16	0.322	0.047	1.9
GV7	CEM III/A	4.5	2.6	0.071	90.57	0.611	0.045	1.5
GV8	CEM II/A-L	4.7	3.9	0.086	60.58	0.596	0.067	2.7

The air content is linked to the number of voids which are detected by the air void analyser. The surface of the aggregate is partly porous with some of the natural material consisting of a combination of porous and non-porous material meaning when the analyser traverses the surface it will add more air content to the total and will cause the final results not to show a true representation. Since the analyser cannot distinguish between what entrapped air, entrained air or a void in the aggregate, the total produced is an overestimation of the actual air content, thus, the air content of the hardened concrete is higher than the fresh.

On the other hand, for the air entrained samples in Table 4.11, the air content of the hardened concrete is lower than the fresh. This is related to the porosity and the absorption of the aggregate. Because of the porosity of the aggregate the water absorption is much higher than for granite (2.2% and 0.8% respectively). Taking a closer look at the microstructure, Table 4.12 lists the voids counted for both non-air entrained and air entrained CEM I containing granite and gravel.

The air content of the hardened concrete for the non-air entrained is higher than the fresh for gravel. The table shows that gravel has a higher air content than granite however the total void count is higher for granite. As shown in Table 4.12 the void count is higher below 60µm, but as previously discussed the void count in this size range does not contribute significantly to the total air content. So, with the void count being higher in the larger voids the air content increases quickly with gravel.

4.2.8 Influence of Different Fly Ashes on the Air Void Characteristics

It has been discussed that fly ash is a difficult material to air entrain and whilst it is possible, trying to maintain the air content for the same material but in a different batch is difficult to achieve. Many attributes affect the behaviour of the material from the carbon content to the fineness and whilst it is possible to air entrain it is very hard to maintain the target air content due the absorptivity of the material.

Figure 4.19 shows the air contents for the fresh and hardened concretes for both non-air and air entrained CEM II/B-V concretes. These concretes are designed for freeze-thaw attack at the maximum possible allowance for replacement content of 35% in accordance with BS 8500. A range of fly ashes were used to look at how the material influences the air void characteristics.

Table 4.13 lists the characteristics determined using the air void analyser and it was observed that the spacing factor for the non-air entrained concretes was lower than the air entrained. Ordinarily, these results would be the other way around with the air entrained concretes having a lower spacing factor due to the increased number of entrained voids. A higher carbon content in the fly ash increases the absorption rate so more admixture is ‘stolen’ by the fly ash.

Table 4.12 Number of voids counted within a class width, percentage difference in void counted and air contents comparison between 40 MPa non-air and air entrained concrete containing granite and concrete containing gravel

Class Width, μm	**Voids Counted**			
	Non-Air Entrained		Air Entrained	
	Granite (M3)	Gravel (GV1)	Granite (M8)	Gravel (GV5)
0-10	366	361	872	528
15-20	221	179	586	278
25-30	97	120	266	156
35-40	79	61	155	111
45-50	52	35	114	87
55-60	45	30	78	76
65-80	70	75	123	114
85-100	43	38	92	72
105-120	25	34	63	64
125-140	21	14	44	31
145-160	12	16	30	16
165-180	7	16	26	18
185-200	2	5	18	20
205-220	2	7	19	9
225-240	3	8	10	11
245-260	3	7	8	8
265-280	2	2	4	5
285-300	0	2	3	11
305-350	3	9	7	12
355-400	3	5	5	4
405-450	3	3	5	7
455-500	1	2	2	3
505-1000	3	5	8	15
1005-1500	1	0	1	1
1505-2000	0	0	1	0
2005-2500	0	0	1	0
2505-3000	0	0	1	0
3005-4000	0	0	0	0
Total Counted	**1060**	**1029**	**2542**	**1651**
Air Content, %	1.9	2.2	4.9	4.0

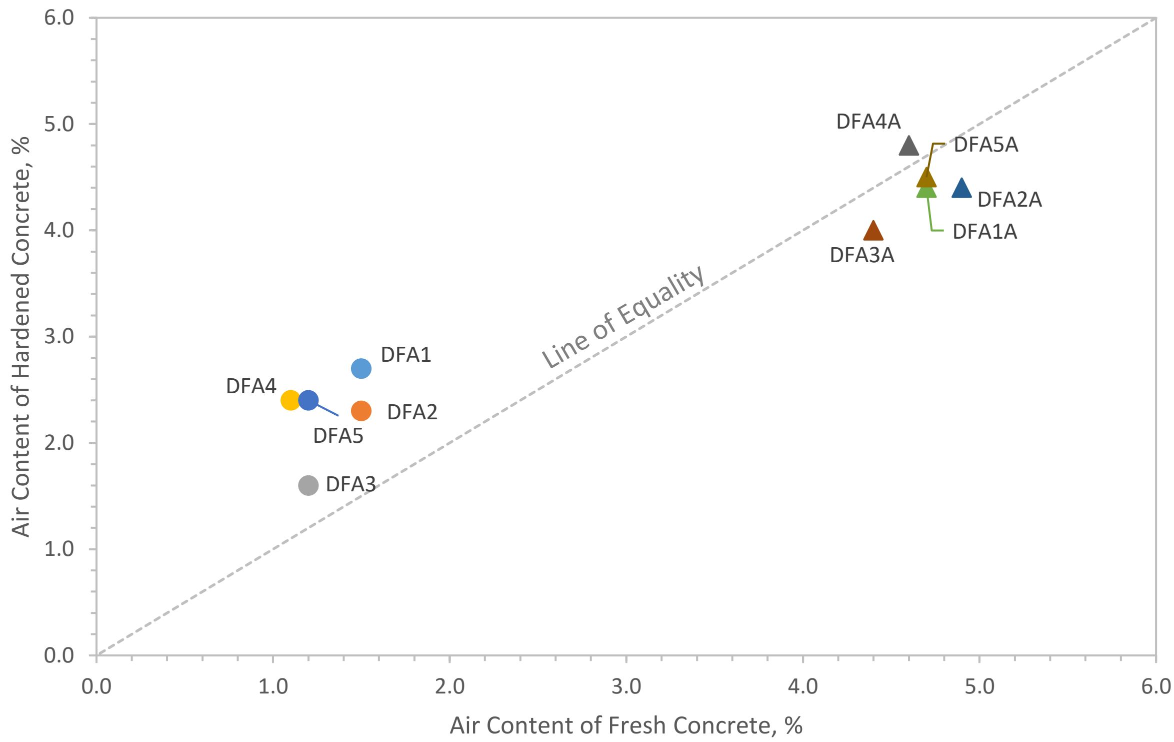


Figure 4.19 Air content of fresh concrete against air content of hardened concrete for various fly ashes tested with a line of equality

Table 4.13 Air void parameters for CEM II/B-V concrete containing different fly ashes determined using the automated air void analyser

Mix Code	Mix Characteristics		Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
	L.O.I, %	Fineness, %							
Non-Air Entrained									
DFA1	4.6	10.5	1.5	2.7	0.082	74.28	0.499	0.054	1.8
DFA2	5.1	8.1	1.5	2.3	0.068	94.52	0.558	0.043	1.4
DFA3	4.1	18.7	1.2	1.6	0.03	241.92	0.997	0.017	1.1
DFA4	5.3	21.2	1.1	2.4	0.048	130.81	0.788	0.031	1.9
DFA5	5.2	25.3	1.2	2.4	0.04	156.62	0.917	0.026	1.6
Air Entrained									
DFA1A	4.6	10.5	4.7	4.4	0.075	67.03	0.74	0.061	3.2
DFA2A	5.1	8.1	4.9	4.4	0.058	84.8	0.917	0.048	3.3
DFA3A	4.1	18.7	4.4	4.0	0.07	74.02	0.737	0.054	2.4
DFA4A	5.3	21.2	4.6	4.8	0.056	84.65	1.007	0.048	3.4
DFA5A	5.2	25.3	4.7	4.5	0.063	76.52	0.869	0.052	3.0

The ambiguous results above are from the difference in the viscosities of the admixtures. Superplasticizer is a viscous liquid compared to air entrainer because of the specific gravity of the two admixtures. With a specific gravity of 1.01 at room temperature, the unburnt carbon can absorb the air entrainer easily reducing the amount available for air entrainment. Superplasticizer has a specific gravity of 1.08 making it more difficult which explains the increased air content for the hardened concrete for the non-air entrained samples due to the side benefits of the superplasticizer being air entrainment.

Concrete uses many different admixtures depending on what the concrete is being for and on many occasions' multiple admixtures. This section looks at investigating how using multiple different admixtures in a single mix affects the air void characteristics.

This method is not always used but instead air entrainer is added to improve the performance for freeze-thaw. Using multiple admixtures in a mix can affect the behaviour of the cement paste and influence the structural properties once hardened. Furthermore, when admixtures are used generally not in combination with others, such as accelerator and viscosity modifier then these can greatly influence the cement paste. Figure 4.20 show the air content for the fresh and hardened concretes of different admixture combinations and Table 4.14 shows the accompanying air void parameters.

4.3 Influence of Admixture Combinations in the Microstructural Properties of Concrete (Phase 2)

From Figure 4.20, there are various air contents for the fresh and hardened concretes recorded which were defined by the different combinations. Combinations AC1 and AC2 are non-air entrained that have higher air contents in the hardened concrete which is a result of the analyser counting the entrapped air because no admixtures are used. AC3 and AC4 only have superplasticizer and whilst different superplasticizers were used both concretes had close fresh and hardened air contents. Similarly, AC7 and AC10 have a superplasticizer and air entrainer and the air contents are very close but slightly higher for the hardened concrete. The other samples have a high air content for the fresh concrete but low for the hardened concrete. This is related to the combinations used but more importantly the compatibility of the admixtures. Admixture suppliers do state that some of their admixtures are compatible with each other but not always.

For these mixes many of the combinations used are admixtures from different suppliers so compatibility is difficult to obtain. Looking at the cluster below the line of equality, AC5 and AC6 have an air entrainer in the concrete but only able to reach 2.0% air content for the hardened concrete. This is due to the air loss through the vibration and compaction. It is important that the concrete is fully compacted so that the strength is assured and ensuring full compaction would be done with a concrete which has a high workability. But in AC5 and AC6 did not have a superplasticizer to increase the workability then the concrete would have been vibrated longer to get good compaction. However, vibrating the concrete too long results in void loss as too many bubbles rise to the surface, thus, a reduction in the hardened air content.

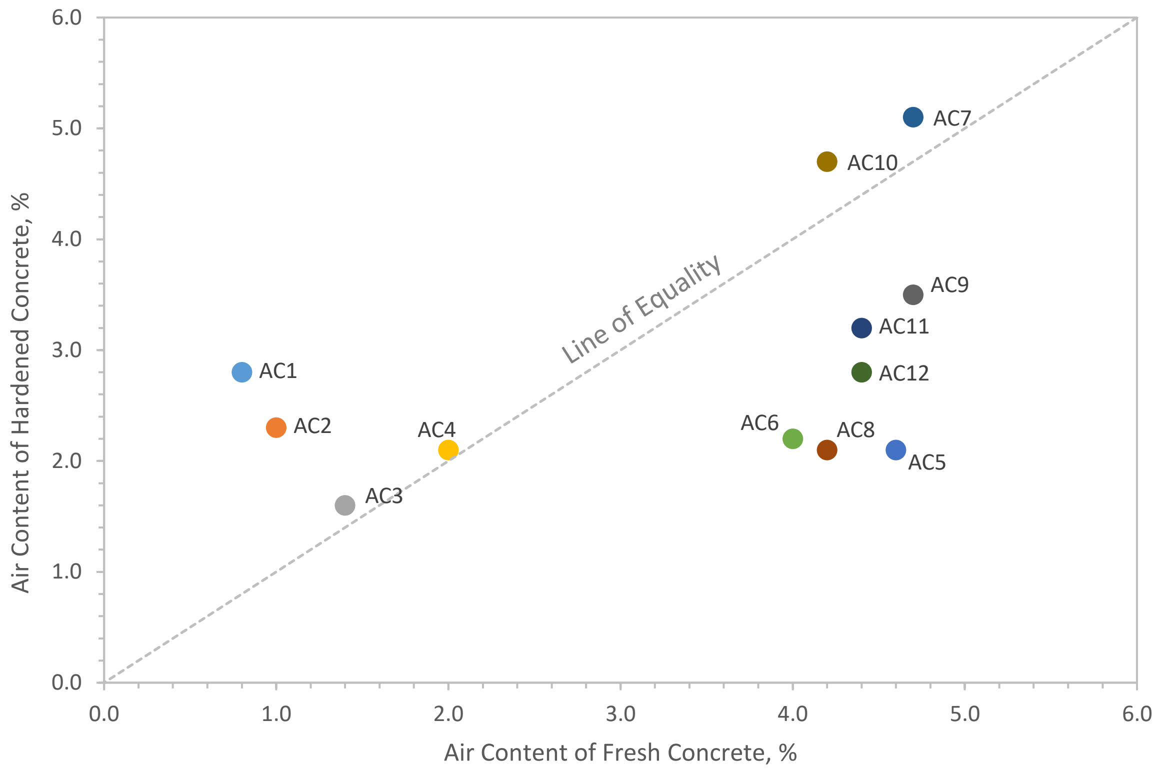


Figure 4.20 Fresh air content plotted against hardened air content for admixture compatibility with a line of equality

Table 4.14 Air void parameters for admixture compatibility determined using the automated air void analyser

Mix Code	Admixture Combination	Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
AC1	No Adm	0.8	2.8	0.077	85.83	0.537	0.052	1.6
AC2	No Adm	1.0	2.3	0.087	77.74	0.425	0.052	1.3
AC3	SP1	1.4	1.9	0.068	106.62	0.464	0.040	1.1
AC4	SP2	2.0	2.1	0.039	174.53	0.926	0.023	1.3
AC5	AE1	4.6	2.1	0.074	97.11	0.524	0.041	1.2
AC6	AE2	4.0	2.2	0.071	111.20	0.613	0.041	1.5
AC7	SP1 + AE1	4.7	5.1	0.087	63.27	0.547	0.064	3.8
AC8	SP1 + AE2	4.2	2.1	0.063	113.48	0.592	0.036	1.3
AC9	SP2 + AE1	4.7	3.5	0.088	65.19	0.579	0.063	2.7
AC10	SP2 + AE2	4.2	4.7	0.077	70.71	0.724	0.064	3.0
AC11	AE1 + ACC	4.4	3.2	0.102	57.97	0.461	0.069	1.6
AC12	AE1 + VMA	4.4	2.8	0.049	139.98	0.953	0.032	1.4

AC8 and AC9 should lie on if not close to the line of equality along with AC7 and AC10 as all these mixes have a superplasticizer and an air entrainer in the concrete. This ties in with the earlier statement about compatibility with the admixtures. AC8 and AC9 have admixtures from different suppliers and as a result they do not work together to provide the voids stability during the hydration process. This suggests chemicals in these combinations are not compatible with each other, though the admixtures use similar base chemicals, it appears that chemicals specific to the admixture do not react as required resulting in a much lower air content.

AC11 and AC12 both include a different admixture from the standard superplasticizer. AC11 includes an accelerator with the air entrainer whilst AC12 used a viscosity modifier (VMA). Figure 4.20 shows that both AC11 and AC12 have the same air content as one another (4.4%) and is very close to the target air content (4.5%) in the fresh state but the difference is in the hardened state. With the aid of the accelerator, AC11 is able to trap in more voids as the accelerator accelerates the hydration process. Despite this advantage the air content of the hardened concrete is lower. This is in relation to the setting time and more importantly the admixture used. The shorter setting time means that when the concrete is being compacted, the bubbles are escaping as they would with any air entrained concrete, but because of the reduced setting time, more bubbles are trapped within the fresh concrete mix.

AC12 combines the use of a VMA with air entrainer. A VMA is used to thicken a mix, typically a self-compacting concrete or concrete cast underwater, to prevent segregation or bleeding because of the number of fines. For AC12 a standard concrete was used and although the hardened air content was much lower than the fresh, it still had a higher air content than AC8. Air loss from AC12 was attributed to the vibrating and compacting of the concrete, but a minor loss compared to AC11 resulting from the thickened mix.

All the AC mixes were designed with a target strength of 40 MPa. The mixes were altered depending on whether they were non-air or air entrained so that the target strength could be reached, and the dosage of the admixtures changed to achieve the target slump and air contents (Class S3 and 4.5% respectively). Varying the admixtures affects both the fresh and hardened properties and one main difference is the compressive strength when compared to the air content. Figure 4.21 shows the air content for the fresh concrete against the compressive strength. As shown, there is a clear separation of the points distinguishing between the air and non-air entrained samples. Collectively, the air entrained data is grouped around the 4.5% air content with different compressive strengths which is related to the admixtures used and the combinations. Similarly, the non-air entrained samples are grouped around the 1.2% air content with slightly wider outliers.

When compared to the air content of the hardened concrete (Figure 4.22) there is a wider dispersion in the data which is difficult to relate. Although the strengths remain the same there is no correlation compared to the fresh air content. This spread would be the result of different admixtures used and how they have influenced the behaviour of the cement paste during the hydration process.

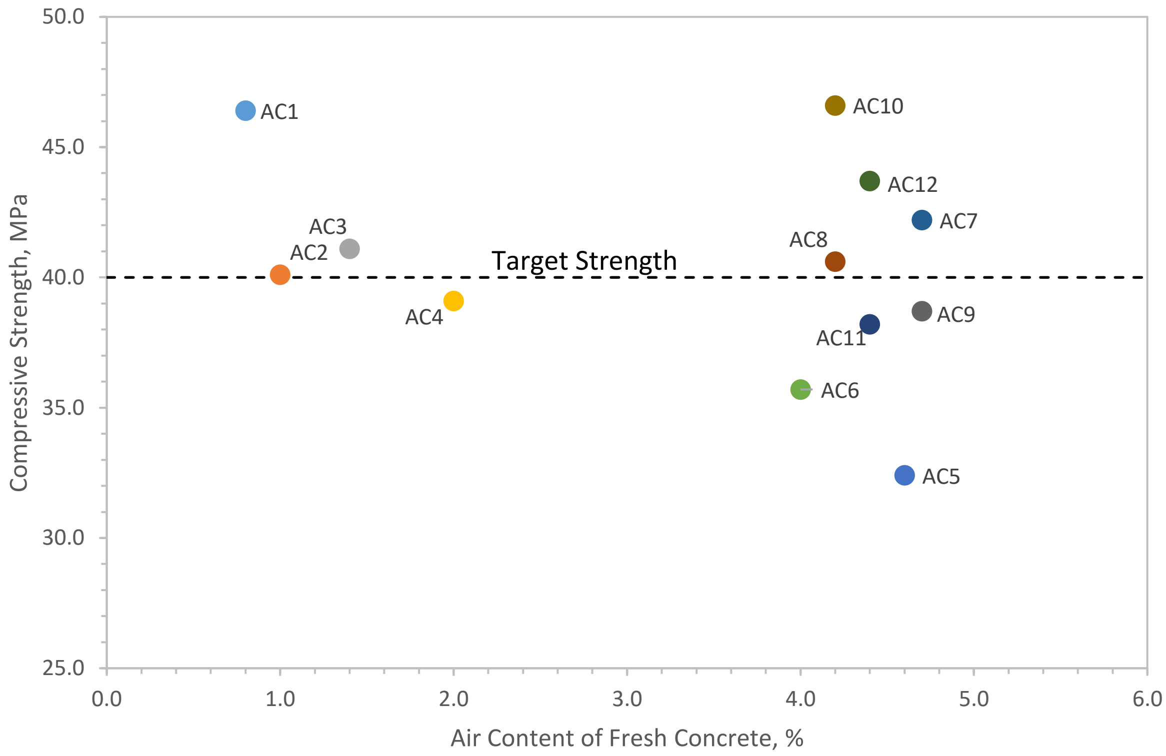


Figure 4.21 Air content of the fresh concrete against the compressive strength for the admixture combinations

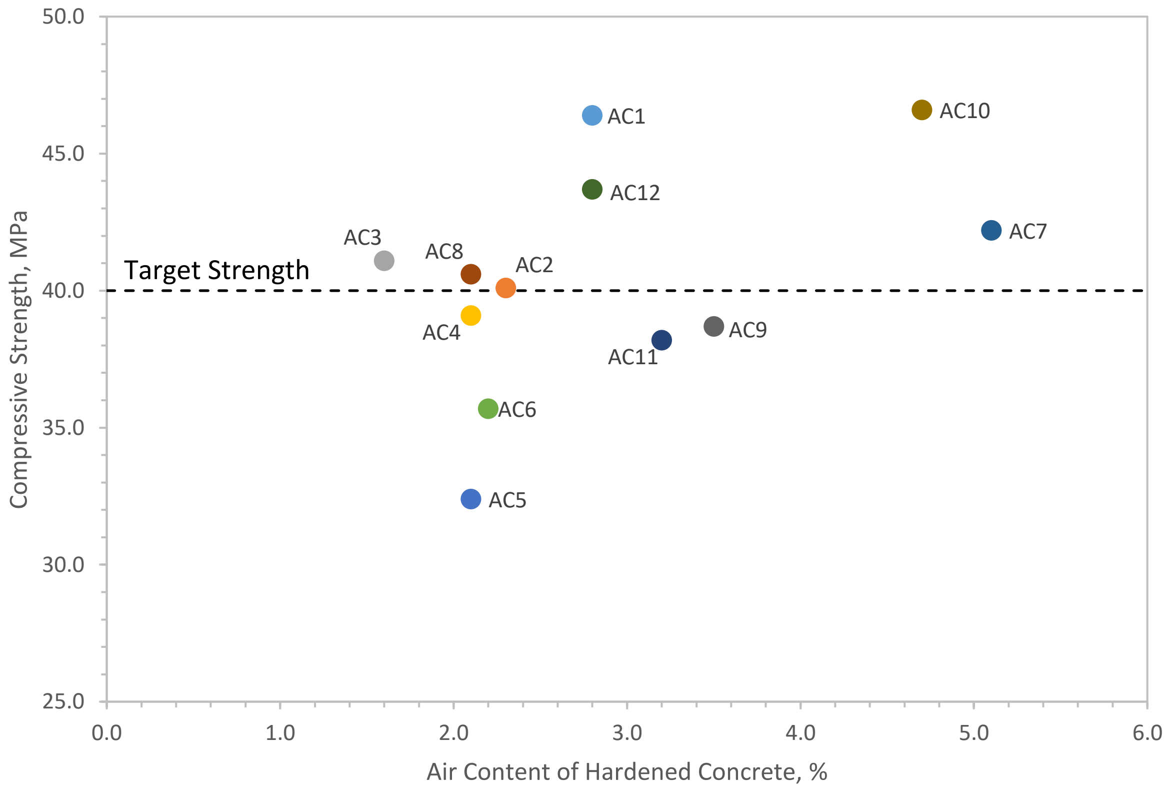


Figure 4.22 Air content of the hardened concrete against the compressive strength for the admixture combinations

Comparing the fresh and hardened air contents (Figure 4.21 and Figure 4.22 respectively) it is shown there is a complete difference in the air content between both. The distribution of the fresh air content values coincides with what was expected from the mix designs with a higher air content for air entrained concretes. What was unexpected was the reduction in the air content of the hardened concrete by comparison. AC5, AC6, AC11 and AC12 all do not have superplasticizer in the mix design potentially affecting the air content due to the concrete being too viscous preventing the air entrained voids from forming a stabilising. The addition of the superplasticizer increases the workability enabling voids to form and folded into the concrete during the mixing process.

Both SP1 and SP2 are poly carboxylic admixtures as the main chemical in the superplasticizer and has been studied to determine the effects on the concrete microstructure. Studies conducted by Lange, et al., (2012) and Huang, et al., (2016) on the influence on the microstructure showed that these types of superplasticizer agents increase the total air content due to excessive foaming when using industrially manufactured poly carboxylate superplasticizers.

When used in concrete mixtures requiring an air content, a defoaming agent can be added to the mix to prevent excessive foaming of the admixtures. Otherwise, continual mixing in the concrete can result in the intended increase in the strength through a reduction in the water/cement ratio which can be lost entirely (Lange. Et al., 2012). However, using a defoamer is very expensive and it should be avoided if possible.

Huang, et al., (2016) reviewed how poly carboxylate (compared to a conventional superplasticizing based on; poly naphthalene, poly melamine and lignosulfonate) influences the microstructure whilst the concrete is subjected to external factors such as carbonation and chloride ingress. They found that using a poly carboxylate, cement pastes have more hydration products providing a denser microstructure and have lower porosity with a smaller critical pore size keeping the fraction of diameter, larger than 100nm lower than when using a conventional superplasticizer.

The use of poly carboxylate superplasticizers suggest that due to the chemistry of the superplasticizer the additional air content observed in the study relates to the ‘extra foaming’ and combining with the air entrainer increases the overall air content leading to the conclusion that poly carboxylate superplasticizers are compatible with other admixtures.

Further study by Lazniewska-Piekarczyk, et al., (2017) reviewed the compatibility of various superplasticizers (with different chemical structures) with air entrainers with cement products. They suggest that in order to ascertain an acceptable workability with the addition of an air entrainer then a poly naphthalene or melamine should be used because using a poly carboxylate can increase the air content by almost three times. This detail proposes there is a chemical(s) in the air entrainer which, when mixed, causes higher foaming in the concrete.

The additional foaming during the mixing process has contributed to the increase in the air content thus, a reduction in the spacing factor in the concretes shown above. Chapter 2 showed that the microbubbles can be subjected to stability issues including collapse or coalescence, however using a poly carboxylate this is not as much of an issue as these newly developed superplasticizers provide a more stable microbubble similar to an air entrainer causing an increase in the air content. It is then a necessity that the air entraining admixture content is reduced slightly to achieve a balance with the superplasticizer.

Research conducted by Al-Neshawy, et al., (2019) studied the influence of three generation of admixture looking at the stability of air content in fresh concretes. They found that for the first and second generation use a concept called electrostatic repulsion (where like charges for example two positive and two negative are placed close to one another) allowing the admixtures to working in the same cement paste (Figure 4.23). Whereas a third-generation superplasticizer creates a steric hindrance, meaning that it stops a chemical reaction due to the shape of the molecule, resulting in the cement grains dispersing (Figure 4.24).

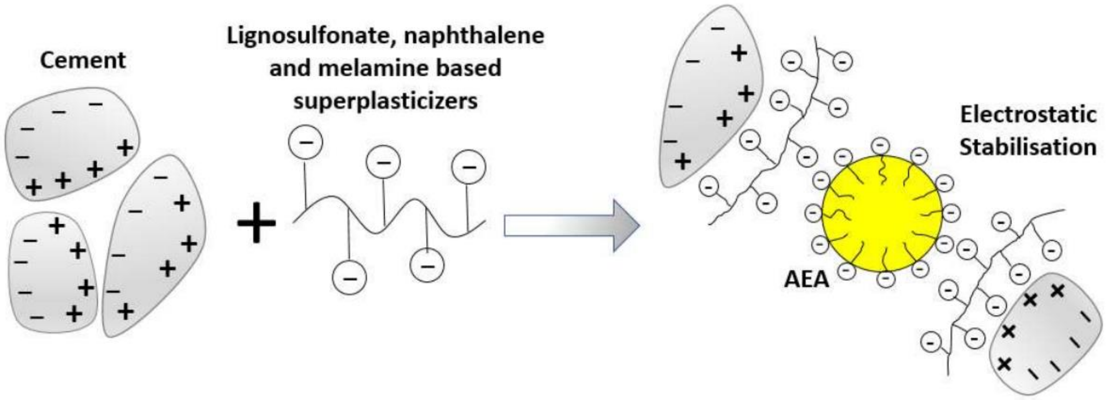


Figure 4.23 Illustration of a first and second generation superplasticizer and the concept of electrostatic repulsion understood to be occurring in a cement and the mechanism of a superplasticizer and air entrainer work within the same cement paste (Al-Neshawy, et al., 2019)

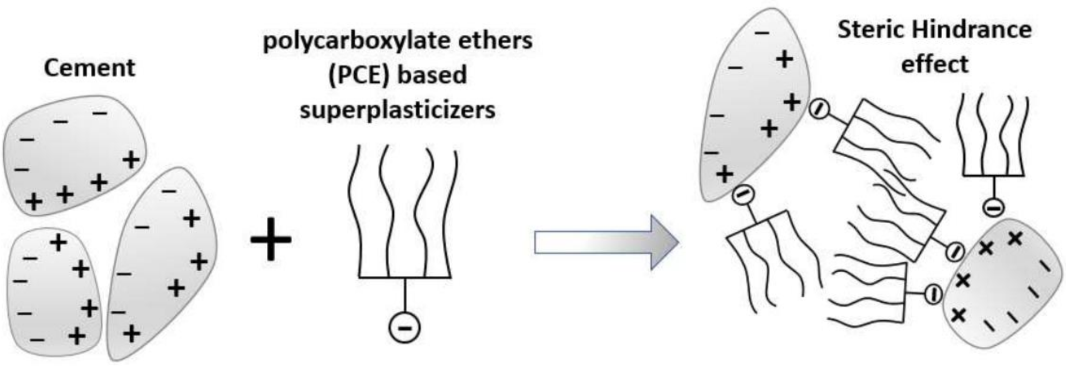


Figure 4.24 Illustration of a third generation superplasticizer and the concept of steric hindrance for a poly carboxylate superplasticizer where there is a potential for cement grain dispersion (Al-Neshawy, et al., 2019)

This section reviewed the compatibility of different admixtures (superplasticizers, air entrainers, accelerator and viscosity modifying admixture) and how they interacted with one another and the cement to provide adequate air content for freeze-thaw durability. Despite the possible problems with the durability of concrete which may occur when certain admixtures mix together, from an air void characteristics perspective the various chemicals in the admixtures do not seem to affect the requirements of the air content or the workability as many of the same admixture types (superplasticizer and air entrainer) have the same chemicals used during the manufacture.

4.4 Comparing Air Void Characteristics of Laboratory Concretes to Industry Concretes (Phase 3)

A series of five industry produced concretes were analysed to determine how the air void characteristics differ from concrete cast in a laboratory. Figure 4.25 shows the plots of fresh and hardened air contents plotted against one another and

Table 4.15 lists the air void parameters. As the figure shows, majority of the concretes lie close to the line of equality apart from M04 which has a higher fresh air content than hardened. Although the air contents are not completely the same, they meet the minimum requirements in accordance with BS 8500.

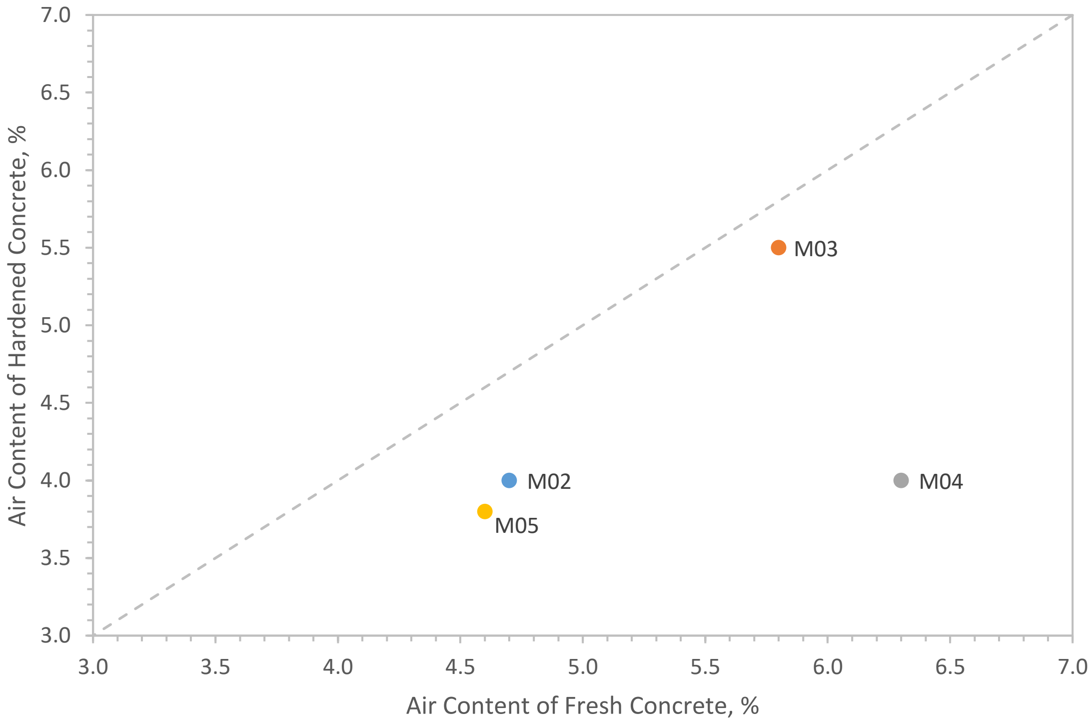


Figure 4.25 Air content for the fresh concrete against the air content for the hardened concrete for the industry produced concretes

Table 4.15 Air void parameters for industry produced concretes determined using the automated air void analyser

Mix Code	Concrete Type	Fresh Air Content, %	Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Micro Air Content, %
M02	CEM I	4.7	4.0	0.046	111.52	1.081	0.038	2.6
M03	CEM III/A	5.8	5.5	0.059	78.97	1.115	0.053	3.5
M04	CEM I	6.3	4.0	0.075	76.0	0.683	0.059	2.1
M05	CEM II/B-V	4.6	3.8	0.067	79.36	0.743	0.052	2.1

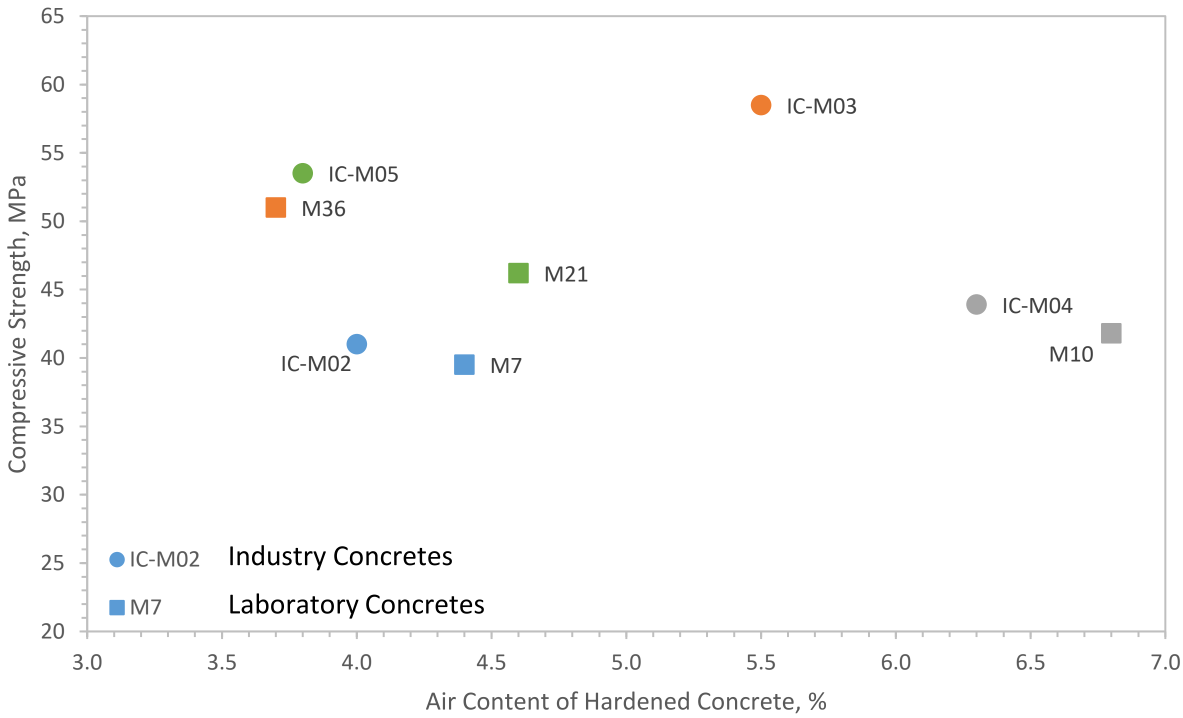


Figure 4.26 Comparison between laboratory and industry produced concretes for the compressive strength of the same cement type against the air content of hardened concrete. The concretes are colour matched showing the concrete comparison with laboratory and industry

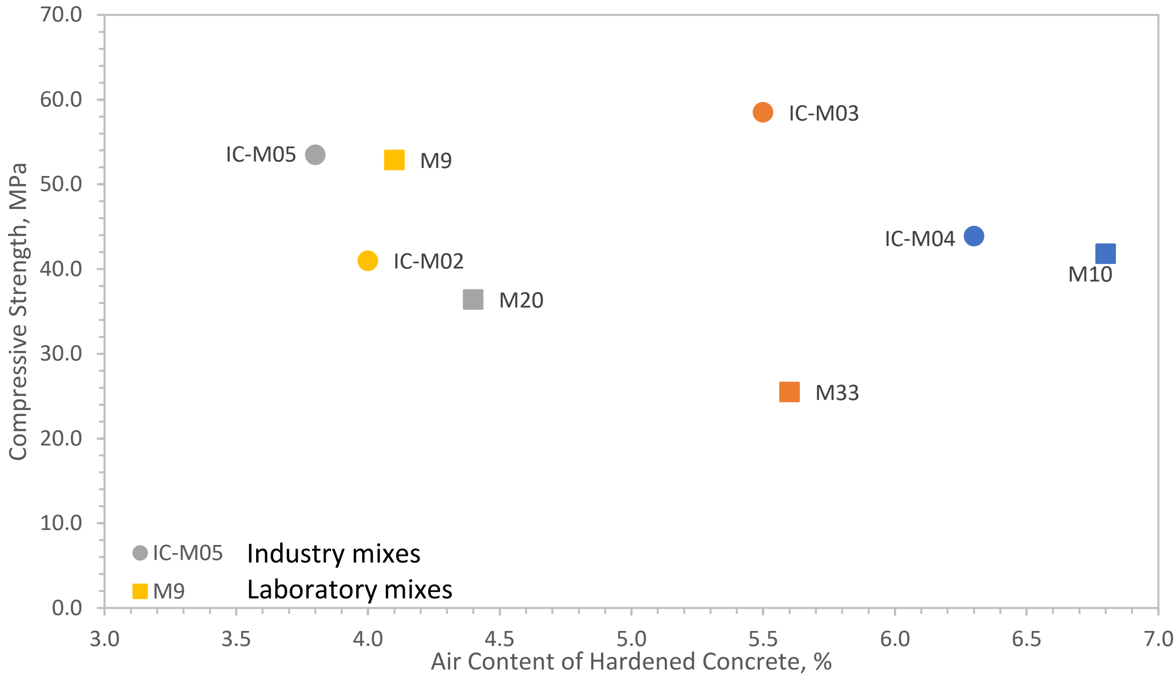


Figure 4.27 Comparison of the air content of hardened concrete of the same cement type between laboratory and industry produced concretes against compressive strength. The concretes are colour matched showing the concrete comparison with laboratory and industry

The air contents there is not much difference between the fresh and hardened industry cast concretes apart from M04 which has a higher fresh air content. Comparing the results to the laboratory concretes, there are major differences but with little correlation. Figure 4.26 shows the laboratory samples against the industry samples with similar compressive strengths. The samples were compared by the compressive strength and the cement type. As shown, there is not much difference between the strengths however the air contents vary especially for M36/M03 with a significant variation of 48%. Table 4.16 shows the results for comparing the industry and laboratory concretes where concrete type and strength are the main comparisons.

Table 4.16 Comparison of air void characteristics between industry and laboratory produced concretes for same concrete type of similar strength

Mix Code	**Concrete Type**	**Compressive Strength, MPa**	**Air Void Characteristics**					
			Hardened Air Content, %	Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Microair Content, %
IC-M02	CEM I	41.0	4.0	0.046	111.52	1.081	0.038	2.6
M7		39.5	5.5	0.059	56.31	0.616	0.071	2.9
IC-M03	CEM III/A	58.5	5.5	0.059	78.97	1.115	0.053	3.5
M36		51.0	3.7	0.093	59.99	0.552	0.068	2.9
IC-M04	CEM I	43.9	4.0	0.075	76.00	0.683	0.059	2.1
M10		41.8	7.5	0.042	87.76	1.675	0.046	5.5
IC-M05	CEM II/B-V/V	58.3	3.8	0.067	79.36	0.743	0.052	2.1
M21		46.2	4.6	0.068	73.48	0.842	0.055	3.2

Changing the main parameter to focus round the air content (Figure 4.26), the relationships between the concretes is similarly spread to that of Figure 4.25. However, using air content as the main parameter does show a difference in the strength distribution when the comparison changes from the air content to the compressive strength of the same cement type.

In a bid to get the best comparison between the differently produced concretes, the laboratory concretes were chosen to closely resemble the industry produced in relation to the compressive strength. Only the air entrained concretes were compared due to all industry concretes tested were air entrained. The analysis of the concretes showed to have significant differences compared to the laboratory concretes in regards to the air void parameters as the concretes produced in industry tend to be a higher strength when air entrained to counteract the compressive strength loss experience with air entrainment (Neville, 2011). Figure 4.28 shows the comparison between the air void parameters (spacing factor, specific surface, void frequency and average chord length) for the laboratory and industry produced concretes which are air entrained and with similar air contents.

Each of the industry produced concretes shown in this section have been matched with a laboratory concrete which closely resembles regarding strength and air content to best review how these differ. As stated, industry increase the strength to reset the balance when strength is lost due to the inclusion of air entrainment, hence, a much higher strength than what was asked for. Furthermore, industry do not put in the maximum amount of replacement material as it is difficult to guarantee the strength requirement as these materials do not provide a high strength themselves without the addition of CEM I. In that instance they ensure that they are within the addition replacement range for that category of cement types to ensure they are in accordance with BS EN 197-1

4.4.1 Spacing Factor

Spacing factor is difficult to compare as it has become less reliable with the development of new admixtures. Industry are constantly changing and developing new admixtures to help improve the environment and save on production costs. From Figure 4.28a there is not a good comparison between the differently produced concretes with IC-M02, IC-M03 and IC-M04 showing a wide distribution in the results which relates to the volume of admixture used. Between the industry produced concretes there is a similarity of AEA used with the average content of 0.1% by weight of cement which would suggest that there should be similar spacing factors. Instead the is a range of different SP contents between 0.36% to 0.6% by weight of cement meaning that the SP is influencing the spacing factor as a result.

Whereas comparing the admixture contents with the laboratory concretes, the results a similar trend in that the SP ranges between 0.37% and 0.6% by weight of cement. However, unlike the industry produced concretes, the laboratory shows to have significantly more dosage with the most being 0.74% for M10 compared to 0.08% for IC-M04 for a similar air content.

IC-M05 shows to have a very good comparison with the spacing factor result being very close. It should be noted that even though the air contents for IC-M05 and M21 were different by 0.8%, it does not mean that it will influence the calculation of the spacing factor as it is dependent on the void size meaning that it is possible to have a lower air content and still maintain the spacing factor provided the bubble sizes remain small but plentiful. Whilst it is not defined what the percentage split is in terms of cement addition, it is assumed that the percentage split for the industry produced concretes would be less than 35% maximum allowance used in the laboratory mixes as the laboratory concretes required an 80% increase in AEA dosage than the industry produced concrete, due to the fly absorbing the AEA.

4.4.2 Specific Surface

The results for the specific surface show that for the industry produced concretes there is a close grouping of the results with each measuring between 75 mm^{-1} and 80 mm^{-1} except for IC-M02 measuring at 111 mm^{-1} due to the higher combination of SP and AEA. M21 and IC-M05 showing a close correlation between the concretes even though M21 has 80% more air entrainer.

The results overall show a similar spread to the spacing factor chart but in reverse suggesting that with a higher spacing factor produces a low specific surface. Again, these results are based on trying to closely resemble laboratory and industry produced concrete regarding the air content and strength and compare the air void parameters as a result. Whilst there is a similar spread to the spacing factor, some of the results are different such as M10 and IC-M04 which have similar strengths and close matching specific surface results even though there is more than nine times the AEA dosage in M10 (laboratory) which can be the related to the increase in the cement content M10 which has an addition 35 kg/m^3 for CEM I (Figure 4.28b).

4.4.3 Void Frequency

The void frequency parameter is determined by counting the number of voids over a traverse length and dividing the total counted by the total length of traverse measured. Most of the results group around the 0.75 mm^{-1} value with one outlier (M10) with a value of 1.6 mm^{-1} which is the result of a high AEA dosage and SP dosage which has been discussed to have air entraining qualities as result from using a poly carboxylate based superplasticizer (Figure 4.28c).

Unlike the specific surface or spacing factor, which both rely on the determination of the air content, the void frequency is independent and can be an indication of a concrete’s future freeze-thaw performance. In this case, although M10 is an outlier it has the potential to perform better than the others due to having a higher number of voids.

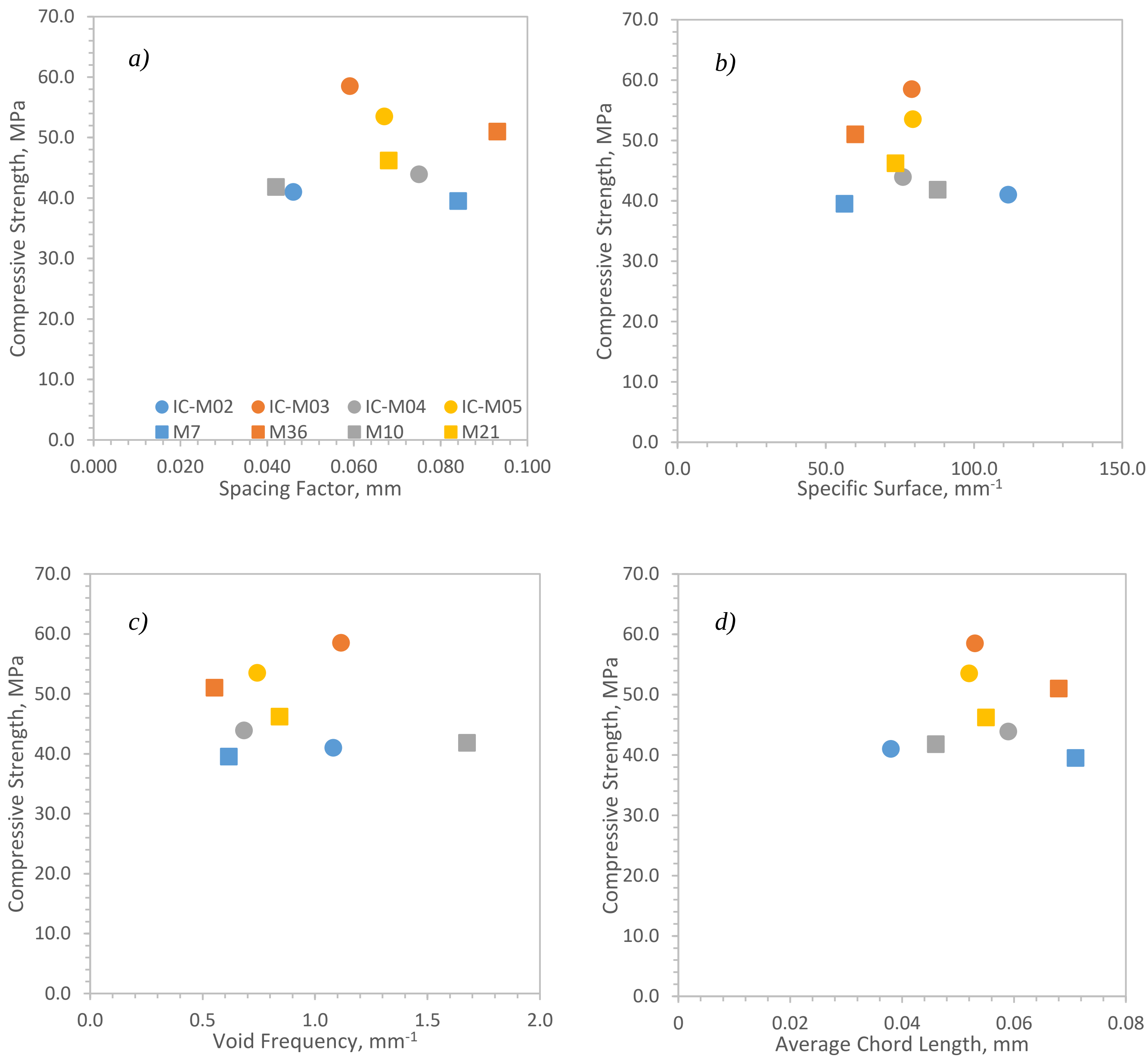


Figure 4.28 Comparison between industry and laboratory concretes of the same cement type with similar compressive strengths and air contents in the hardened state comparing the air void characteristics for a) spacing factor; b) specific surface; c) void frequency and; d)average chord length to the compressive strength. The concretes are colour matched showing the concrete comparison with laboratory and industry

4.4.4 Average Chord Length

It is difficult to use the average chord length when reviewing a concrete's capability to resist freeze-thaw as the results are not easily interpreted. Depending on the cement type, admixture used, and the dosage would determine the number of voids and size within the concrete, thus, the average chord length (bubble size). In theory, if there are enough bubbles within the concrete the results in Figure 4.28d would converge on or around a similar chord length and since the development of different admixture with additional benefits it makes it more difficult to determine what is and is not air entrained.

The results show that there is a range of 38μm to 70μm in size for both concrete producers with M21 and IC-M05 showing a close approximation to each other. The smallest average chord is 38μm for IC-M02, a result from the higher dosages of both SP and AEA.

4.5 Comparison Between ASTM C457 and BS EN 480-11 Air Void Analysis Test Methods

During this research project there have been two standards relating to how the air void characteristics were calculated. The automated air void analyser provides the user both options when the analysis is being carried out. This section looks to perform a comparison between the two standards in a bid to determine whether each standard provides accurate results, or the parameters outlined before analysis affect the resulting outcomes.

Outlined in Table 2.12 are the equations used to determine the parameters. For the main parameters such as the air content, specific surface and spacing factor the equations are relatively similar with some differences being the labelling of the variables. In terms to the calculation and the system at which they are determined is the same for both standards.

Looking at Table 4.17 and Table 4.18, the layout of the results are different in comparison. The ASTM results table (Table 4.17) is mainly focussed on the air content and accumulation of air contents for each of the void sizes to produce the total air content. Columns 1 and 2 are the same for both the results tables but afterwards the tables display the results differently. Columns 3 and 4 in the table look at the total void count for the void size and changing the value into a percentage of the overall void count. Columns 5 and 6 are the percentages of the air content for each of the void sizes and the cumulative air content of the specimens.

BS EN results portray more than just simply the air contents of the specimens. Table 4.18 shows how the results for BS EN 480-11 are laid out. As with ASTM, the first and second columns show the void size range and the number of voids counted within that range. After that the columns change to give more detailed results. Column 4 totals the number of voids (for a particular range) divided by the total length of the traverse to produce a total length of air intercepted for a void size. Column 5 is the possible fraction of voids that will be counted. Column 6 is the total number of voids per mm^3 which contains a certain void size. Column 7 is the total number of voids which have a diameter that is equal to the upper limit of the void range. Column 8 is the volume of each of the voids in a particular class. Columns 9 and 10 are the air contents for each of the void ranges and the cumulative air content respectively.

BS provides a detailed spreadsheet of the air void results with attention being made to the air content as a whole and to each individual class size detailing the void volumes, chord frequency and possible totals per mm^3 for each class. Although the detail of the results is very good, ASTM provides a basic results spreadsheet which allows the user to pinpoint the required values almost instantly rather than spending time trying to find the values.

Air void characteristics are determined to analysis the microstructure of the concrete to understand and develop ways to better protect against external factors. One result which is not displayed or considered in ASTM is the micro air content where majority of the air voids reside within. Typically, there should be a high number of small voids to allow water to flow into multiple locations quickly so by the time the freezing cycle occurs, the water has only partially filled the voids leaving enough room for the ice to expand without damaging the concrete.

If the microair content was considered for both standards, then the results would be 4.1% for ASTM and 3.5% for BS EN. These results show a 0.6% difference between them which is not much but with the standards carrying out the same calculations the results should be the same if not very close. What has been observed between the tables is the void ranges listed in column 2. ASTM shows a consistent numbering for example; 10-20µm then 20-30µm as shown in Table 4.17. However, BS does not have the same range system to account for all the void sizes. Instead, rather than using the real air void distribution the standard uses a calculated air void distribution where BS uses a rounding system to the nearest 5µm (15-20µm then 25-30µm) which allows an easier calculation to be done.

Using this method does allow for an easier calculation however the final characteristic results (air content, spacing factor, specific surface, micro air content) are not as accurate as they would be and from the tables above there are differences between the results. Table 4.18 shows a comparison of all the parameters calculated for each to the void ranges.

As shown in Table 4.19 the results for each standard are different. Because BS implements a calculated air void distribution rather than using the real distribution then it may be possible that either voids were miss counted or were not counted at all or the calculation has placed voids into a different class from where they are actually supposed to be in. Comparing the standards in Table 4.19 there are notable differences in the air contents especially up to 30µm where the number of voids counted are significantly different. This would then be related to the calculated air void distribution which would possibly have class many of the voids in the wrong void class. Although there are differences in the cumulative air contents for both test methods the final results are very similar by comparison showing a 0.28% difference between the air contents.

Table 4.17 Air void distribution according to ASTM C457 for CEM I air entrained concrete at 40 MPa strength (M8)

Column	1	2	3	4	5	6
Subject	**Class**	**Chord Size**	**Recorded Number of Chords in Class**	**Number of Chords in Percent**	**Air Content in Class**	**Cumulative Air Content**
Units		**μm**		**%**	**%**	**%**
	1	0-10	640	25.18	0.24	0.24
	2	10-20	744	29.27	0.48	0.72
	3	20-30	298	11.72	0.325	1.045
	4	30-40	165	6.49	0.25	1.295
	5	40-50	124	4.88	0.24	1.535
	6	50-60	84	3.3	0.2	1.735
	7	60-80	129	5.07	0.39	2.125
	8	80-100	97	3.82	0.38	2.505
	9	100-120	62	2.44	0.3	2.805
	10	120-140	43	1.69	0.24	3.045
	11	140-160	32	1.26	0.205	3.25
	12	160-180	28	1.1	0.2	3.45
	13	180-200	18	0.71	0.15	3.6
	14	200-220	20	0.79	0.18	3.78
	15	220-240	10	0.39	0.1	3.88
	16	240-260	8	0.31	0.08	3.96
	17	260-280	4	0.16	0.045	4.005
	18	280-300	4	0.16	0.05	4.055
	19	300-350	7	0.28	0.095	4.150
	20	350-400	5	0.2	0.08	4.23
	21	400-450	5	0.2	0.08	4.31
	22	450-500	2	0.08	0.03	4.34
	23	500-1000	9	0.35	0.24	4.58
	24	1000-1500	1	0.04	0.025	4.605
	25	1500-2000	1	0.04	0.085	4.69
	26	2000-2500	1	0.04	0.1	4.79
	27	2500-3000	1	0.04	0.06	4.85
	28	3000-4000	0	0.0	0.0	4.85

Table 4.18 Air void distribution according to BS EN 480-11 for CEM I air entrained concrete at 40 MPa strength (M8)

Column	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Subject	**Class**	**Class Width**	**Recorded Number of Chords in Class**	**Chord Frequency**	**Fraction Encountered**	**Possible Total**	**Voids in Class**	**Void Volume**	**Air Content**	**Cumulative Air Content**
Units		**μm**		**mm^{-1}**	**mm^2**	**mm^{-3}**	**mm^{-3}**	**mm^3**	**%**	**%**
	1	0-10	872	0.38145	0.0001178	3238.13513	2305.64	5.24×10^{-7}	0.121	0.12
	2	15-20	586	0.25634	0.0002749	932.4953	663.142	4.19×10^{-6}	0.278	0.4
	3	25-30	266	0.11636	0.0004320	269.3529	154.236	1.41×10^{-5}	0.217	0.62
	4	35-40	155	0.06780	0.0005890	115.11719	48.278	3.35×10^{-5}	0.162	0.78
	5	45-50	114	0.04987	0.0007461	66.83925	29.062	6.54×10^{-5}	0.19	0.97
	6	55-60	78	0.03412	0.0009032	37.77761	14.158	1.13×10^{-4}	0.16	1.13
	7	65-80	123	0.05381	0.0022780	23.61974	9.771	2.68×10^{-4}	0.262	1.39
	8	85-100	92	0.04024	0.0029060	13.84892	6.051	5.24×10^{-4}	0.317	1.71
	9	105-120	63	0.02756	0.0035340	7.79826	3.175	9.05×10^{-4}	0.287	1.99
	10	125-140	44	0.01925	0.0041630	4.62349	1.884	1.44×10^{-3}	0.271	2.27
	11	145-160	30	0.01312	0.0047910	2.73917	0.64	2.14×10^{-3}	0.137	2.4
	12	165-180	26	0.01137	0.0054190	2.09883	0.797	3.05×10^{-3}	0.243	2.65
	13	185-200	18	0.00787	0.0060470	1.30214	0.057	4.19×10^{-3}	0.024	2.67
	14	250-220	19	0.00831	0.0066760	1.24498	0.646	5.58×10^{-3}	0.361	3.03
	15	225-240	10	0.00437	0.0073040	0.59891	0.158	7.24×10^{-3}	0.114	3.14
	16	245-260	8	0.0035	0.0079330	0.44114	0.237	9.02×10^{-3}	0.218	3.36
	17	265-280	4	0.00175	0.0085610	0.20439	0.062	1.15×10^{-2}	0.071	3.43
	18	285-300	3	0.00131	0.0091890	0.14282	0.024	1.41×10^{-2}	0.034	3.47
	19	305-350	7	0.00306	0.0257200	0.11906	0.045	2.24×10^{-2}	0.101	3.57
	20	355-400	5	0.00219	0.0296500	0.07377	0.009	3.35×10^{-2}	0.029	3.6
	21	405-450	5	0.00219	0.033580	0.06513	0.042	4.77×10^{-2}	0.199	3.8
	22	455-500	2	0.00087	0.037500	0.02333	0.017	6.54×10^{-2}	0.114	3.91
	23	505-1000	8	0.0035	0.5910000	0.00592	0.005	5.24×10^{-1}	0.287	4.2
	24	1005-1500	1	0.00044	0.9830000	0.00045	0.0	1.77	0.022	4.22
	25	1505-2000	1	0.00044	1.3760000	0.00032	0.0	4.19	0.03	4.25
	26	2005-2500	1	0.00044	1.7690000	0.00025	0.0	8.18	0.037	4.29
	27	2505-3000	1	0.00044	2.1620000	0.0002	0.0	1.41×10^{1}	0.285	4.57
	28	3005-4000	0	0.0	5.5020000	0.0	0.0	3.35×10^{1}	0.0	4.57

Table 4.19 Comparison between the air void calculations for ASTM C457 and BS EN 480-11 for an air entrained CEM I concrete (M8)

	ASTM C457				BS EN 480-11			
Subject	Class	Chord Size	Recorded Number of Chords in Class	Cumulative Air Content	Class	Class Width	Recorded Number of Chords in Class	Cumulative Air Content
Units		µm		%		µm		%
	1	0-10	640	0.24	1	0-10	872	0.12
	2	10-20	744	0.72	2	15-20	586	0.4
	3	20-30	298	1.045	3	25-30	266	0.62
	4	30-40	165	1.295	4	35-40	155	0.78
	5	40-50	124	1.535	5	45-50	114	0.97
	6	50-60	84	1.735	6	55-60	78	1.13
	7	60-80	129	2.125	7	65-80	123	1.39
	8	80-100	97	2.505	8	85-100	92	1.71
	9	100-120	62	2.805	9	105-120	63	1.99
	10	120-140	43	3.045	10	125-140	44	2.27
	11	140-160	32	3.25	11	145-160	30	2.4
	12	160-180	28	3.45	12	165-180	26	2.65
	13	180-200	18	3.6	13	185-200	18	2.67
	14	200-220	20	3.78	14	250-220	19	3.03
	15	220-240	10	3.88	15	225-240	10	3.14
	16	240-260	8	3.96	16	245-260	8	3.36
	17	260-280	4	4.005	17	265-280	4	3.43
	18	280-300	4	4.055	18	285-300	3	3.47
	19	300-350	7	4.150	19	305-350	7	3.57
	20	350-400	5	4.23	20	355-400	5	3.6
	21	400-450	5	4.31	21	405-450	5	3.8
	22	450-500	2	4.34	22	455-500	2	3.91
	23	500-1000	9	4.58	23	505-1000	8	4.2
	24	1000-1500	1	4.605	24	1005-1500	1	4.22
	25	1500-2000	1	4.69	25	1505-2000	1	4.25
	26	2000-2500	1	4.79	26	2005-2500	1	4.29
	27	2500-3000	1	4.85	27	2505-3000	1	4.57
	28	3000-4000	0	4.85	28	3005-4000	0	4.57

4.6 Summary of Chapter 4

Before freeze-thaw testing was conducted, it was theorised by Powers that concrete resistance to freeze-thaw can be predicted based on the internal microstructure of the concrete. This led to the creation of the Powers spacing factor parameter that anticipates a concrete's freeze-thaw performance based on the measured distance between voids. The parameter provided an approximation as to how the concrete would react to freeze-thaw depending on the spacing of its voids, the closer they were the better protected the concrete. However, due to developments of new admixtures including superplasticizers and air entrainers, the spacing factor parameter has now become less viable as a parameter to approximate a concrete's durability simply because using only superplasticizers in concrete creates voids due to its side benefit of having air entraining qualities.

This chapter has reviewed the microstructural air void characteristics of the internal concrete structure including the air content, spacing factor, specific surface, void frequency and microair content. Concrete samples were varied in compressive strength, cement type and air content and the internal structure analysed using automated air void analysis to determine the parameters and compare them to one another in a bid to refine the freeze-thaw resistance of a concrete before conducting destructive tests. Recently, the introduction of automated analysis for determining the air void characteristics has sped up the analysis process. What used to take up to 6 hours to complete by hand per sample can now be done in 20 minutes.

The continual development of admixtures for concrete has caused secondary benefits in concrete. Namely superplasticizer provides some air entrained due to the poly carboxylate chemical used in third generation admixtures to increase forming. Whilst it does provide additional foaming increasing the air content it also influences the microstructural properties. Spacing Factor is known to be the deciding parameter for identifying a freeze-thaw resistant concrete, however as the results show above the parameter claims that a (target strength) 20 MPa CEM II/B-V non-air entrained concrete has the capacity to withstand freeze-thaw when in fact CEM II/B-V exceed the 1.0kg/m^2 limit. Furthermore, the data considers that some of the non-air entrained concrete would perform better than air entrained concretes based on the Spacing Factor result, for example, M31 (50 MPa non-air entrained CEM III/A concrete) has a Spacing Factor value of 0.083 mm whereas M36 (50 MPa air entrained CEM III/A concrete) has a Spacing Factor of 0.093 mm stating that although should provide an *Acceptable* scaling rating, M31 will have a lower scaling loss despite M36 being an air entrained concrete so the Spacing Factor does not work in that regard.

Both standards produce the same parameter results except for the microair content which is only calculated in BS EN 480-11. Microair content is a relatively new concept that calculates the total air content of void measuring 300µm or less in diameter. Included only in BS EN 480-11, the parameter presents the total air content for the *optimum* void size range to reduce freeze-thaw damage. Consequently, this parameter only provides the total air content to a certain diameter size and whilst that can be a positive initially when considering the minimum void size requirement to prevent freeze-thaw then causes issues. Namely the influence on other parameters including the spacing factor which is affected by the high proportion of void less than 30 µm. For example, M8 (from Table 10) shows the total voids counted from the sample and when calculated the total voids for the first 0-30m account for 67.8% of the total counted voids greatly influencing the other parameters. Instead of just the microair content there should be an *optimum air content* which determines the air content for an effective entrained air void group.

Industry produced concretes were compared to those produced in the laboratory to review the differences between the concretes regarding the air void parameters. Laboratory concretes were selected for comparison based on the cement type, compressive strength and air content which best matched the industry concretes for comparison. From the results, it was observed that there was little correlation between the results for all the parameters but what was noticed was that the dosage of air entrainer had significantly increased (approximately 80% more) suggesting that the industry produced concretes were not using as much replacement CEM I material compared to the laboratory concretes keeping the dosage used to a minimum.

The analysis throughout this chapter reviewed the all the characteristics and their advantages and disadvantages regarding the determination of a concrete's freeze-thaw ability. Overall, it can be said that the use of only the spacing factor as a means of predicting a concrete's freeze-thaw performance is now less viable due to developing admixtures. Instead parameters such as the spacing factor and void frequency should now be used in tandem to determine a concrete's durability with the spacing factor used as a final reference before experimental testing.

Chapter 5
Influence of Cement and Aggregate Types on Freeze-Thaw Resistance

5.1 Introduction

The introduction of various cement types in concrete has led to a range of durability testing to understand how these concretes resist different environmental factors in the field. With more structures using alternative cement types rather than CEM I, there is a need to assess these materials for suitability for different situations. Freeze-thaw is a major deterioration mechanism and the test determines the choice of concretes used in cold climates. Testing for freeze-thaw salt scaling in Europe is conducted using CEN/TS 12390-9 which is the European standard for testing concrete for freeze-thaw durability.

In Phase 1a, different properties of the concrete influences its durability in freeze-thaw conditions such as the target strength, cement type and replacement content and air content. Freeze-thaw data combined with the air void analysis results produced in Chapter 4 have been analysed to determine the performance of all the concretes cast to understood how the concrete microstructure is characterised and how concrete may be able to withstand freeze-thaw attack.

Phase 2 of the experimental programme considers the influence of admixture compatibility on the microstructure (Chapter 4) and the freeze-thaw durability (Chapter 5). Focusing on air entrainer combined with superplasticizer, accelerator and viscosity modifying admixture (VMA), these admixtures were combined within mixes to identify how the microstructure is affected, thus, influencing the protection against freeze-thaw attack. However, many of the admixtures used in concrete were only designed to work with CEM I, but now with a range of replacement materials available tied with sustainability agendas from the European Union to reduce CO_2 emissions, require the admixtures to be compatible with not only each other but with the cement type.

5.2 Freeze-Thaw Scaling of Air and Non-Air Entrained Concretes with Different Target Strengths (Series 1 and 2)

In Series 1 and 2, four cement types were cast (CEM I, fly ash, GGBS and limestone) varying the target strength from 20 MPa to 60 MPa for both entrained and non-air entrained concretes to identify which could withstand freeze-thaw attack. Ordinarily, when concrete has the addition of air entraining admixture (AEA) there is a reduction in the compressive strength. At the same time a higher strength rather than the inclusion of AEA would give a similar result however that result itself is dependent on several factors including the target strength and the cement type.

Figure 5.1 illustrates entrained and non-air entrained CEM I concretes with various target strengths under freeze-thaw conditions. All the air entrained concretes (M6 – M9) achieve a minimum good scaling rating at 56 cycles (Sn_{56}) even though M6 and M7 do have higher mass loss this could be attributed to the lower strength. Considering that when the air entrained concretes compressive strength increases the amount of scaling decreases in direct proportion until a strength is reached where little to no scaling loss occurs, although this dependent on the cement type used as each varies. Figure 5.1 shows that an air entrained concrete with a 50 MPa target strength is the point where increasing the strength further would only further reduce the scaling loss with the increase in the cement contain as M5 shows with a target strength of 60 MPa.

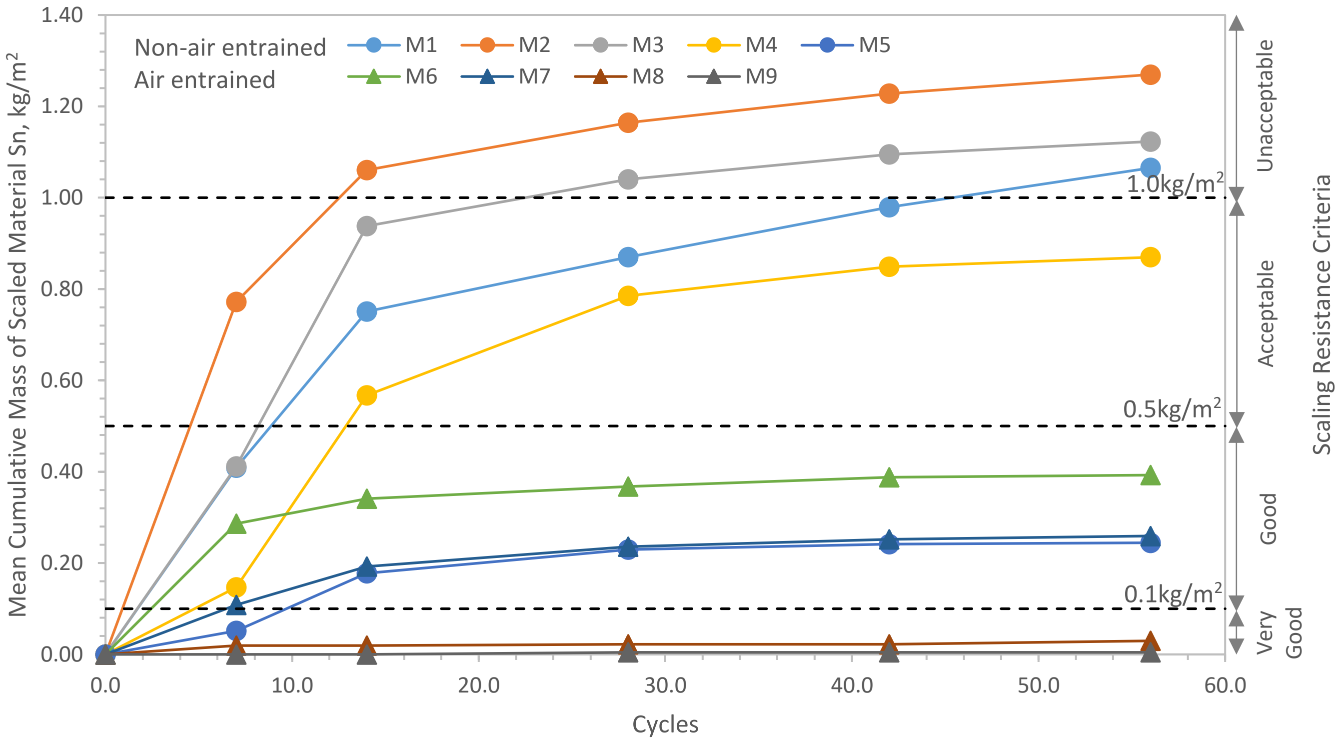


Figure 5.1 Freeze-thaw scaling of CEM I Series 1 and 2 concretes with the scaling resistance criterion detailed in SS 137244

From Figure 5.1 and Table 5.1, M2 and M3 are shown to have a higher mass loss than M1. Ordinarily it would be other way round because with the increase in the strength, the total scaled material loss decreases as a result. This is down to the silicon sealant around the outside of M1 which seals the rubber wrap around the outside of the sample and the top of the concrete (Figure 5.2). With the cycling of temperatures between +23 °C and -18 °C the silicon sealant expands and contracts pulling on the weak outer layer of the concrete. This, combined with the low strength, leads to the concrete cracking early and quickly during the test meaning that around the edges the silicon pulls the concrete away allowing the salt solution to drain off. Because the solution has drained off, there is little deterioration of the test surface.

Table 5.1 Scaling criteria results for CEM I Series 1 and 2 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration and confidence limit for each mix

Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m^2/cycle	Confidence Limit, ± kg/m^2	[1]Scaling Criteria
	Actual Strength, MPa	w/c	Air Content, %						
Non-Air Entrained									
M1	29.0	0.75	1.2	1.07	42 – 56	1.22	0.2967ln(x)	0.32	Unacceptable
M2	38.4	0.63	1.2	1.27	7 – 14	1.09	0.2279ln(x)	0.99	Unacceptable
M3	49.7	0.54	1.6	1.12	14 – 28	1.08	0.3171ln(x)	0.34	Unacceptable
M4	59.5	0.46	1.8	0.87	na	1.11	0.3438ln(x)	1.13	Acceptable
M5	69.9	0.4	1.7	0.24	na	1.06	0.0903ln(x)	0.25	Good
Air Entrained									
M6	30.5	0.63	4.5	0.39	na	1.07	0.0508ln(x)	0.51	Good
M7	39.5	0.52	4.3	0.26	na	1.10	0.0714ln(x)	0.05	Good
M8	47.8	0.45	4.2	0.03	na	1.33	0.0041ln(x)	0.03	Very Good
M9	52.9	0.4	4.7	0.0	na	1.00	0.0026ln(x)	0.00	Very Good

na – not applicable
[1]In accordance with SS 137244

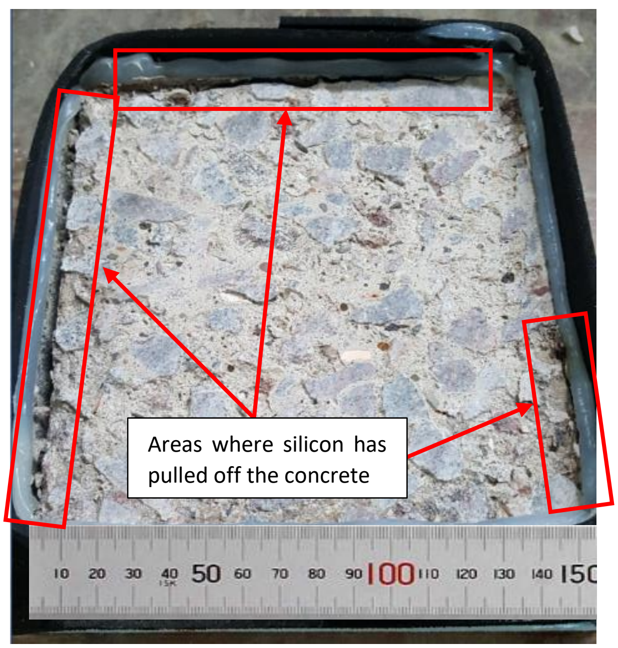


Figure 5.2 20 MPa CEM I non-air entrained concrete (M1) showing the silicon sealant pulling off the edges of the sample preventing water to pond on the surface

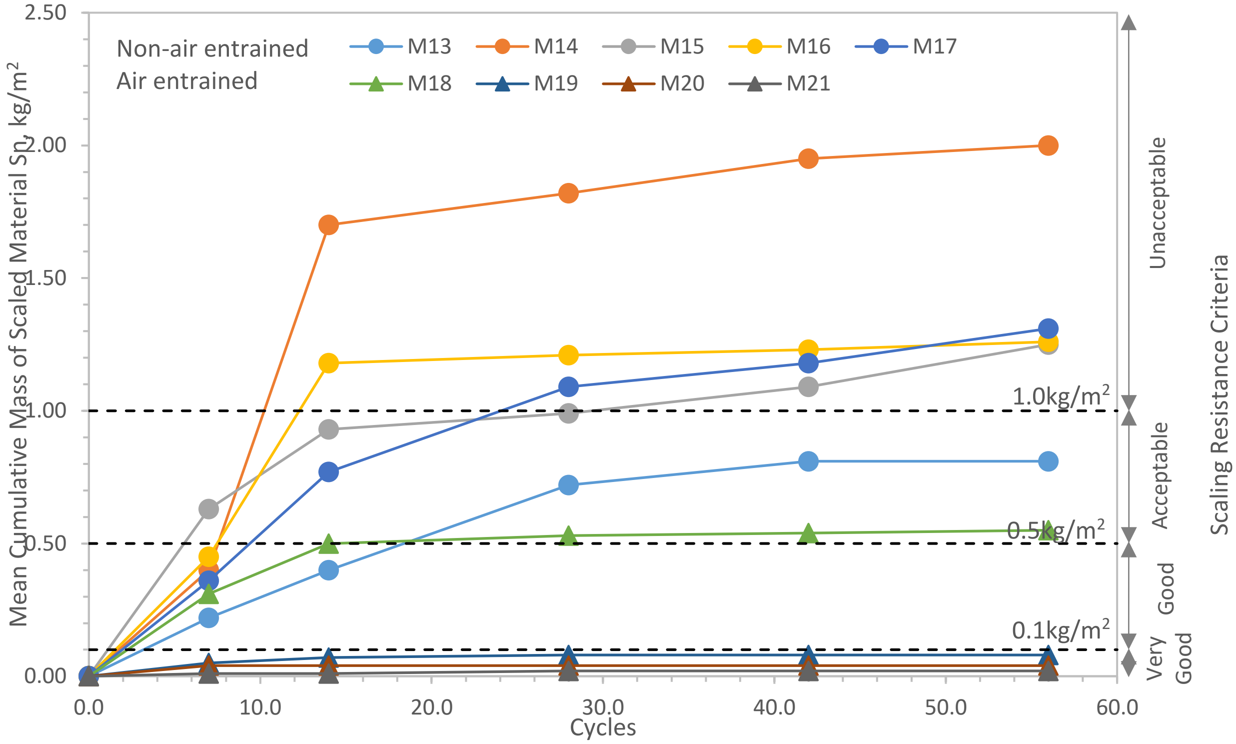


Figure 5.3 Freeze-thaw scaling of CEM II/B-V Series 1 and 2 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.2 Scaling criteria results for CEM II/B-V Series 1 and 2 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit Sn≥1.0kg/m^2	Sn_{56}/ Sn_{28}	Rate of Deterioration kg/m^2/cycle	Confidence Limit, ± kg/m^2	[1]Scaling Criteria
	Actual Strength, MPa	w/c	Air Content, %						
Non-Air Entrained (Series 1)									
M13	22.7	0.66	1.0	0.81	na	1.13	0.3112ln(x)	0.99	Acceptable
M14	27.4	0.56	1.3	2.00	7 – 14	1.10	0.6964ln(x)	1.73	Unacceptable
M15	39.4	0.47	1.5	1.25	28 – 42	1.26	0.2626ln(x)	0.42	Unacceptable
M16	49.7	0.4	1.6	1.26	7 – 14	1.04	0.3419ln(x)	0.44	Unacceptable
M17	60.0	0.35	1.8	1.31	14 – 28	1.20	0.4475ln(x)	1.19	Unacceptable
Air Entrained (Series 2)									
M18	21.8	0.56	4.4	0.55	na	1.06	0.1053ln(x)	0.41	Acceptable
M19	29.8	0.46	4.3	0.08	na	1.00	0.0142ln(x)	0.07	Very Good
M20	36.4	0.4	4.7	0.04	na	1.00	[2]0.04	0.00	Very Good
M21	46.2	0.35	4.5	0.02	na	1.00	0.0059ln(x)	0.01	Very Good

na – not applicable [1]In accordance with SS 137244

[2]M20 has no equation due to no further material loss after first 7 cycle test

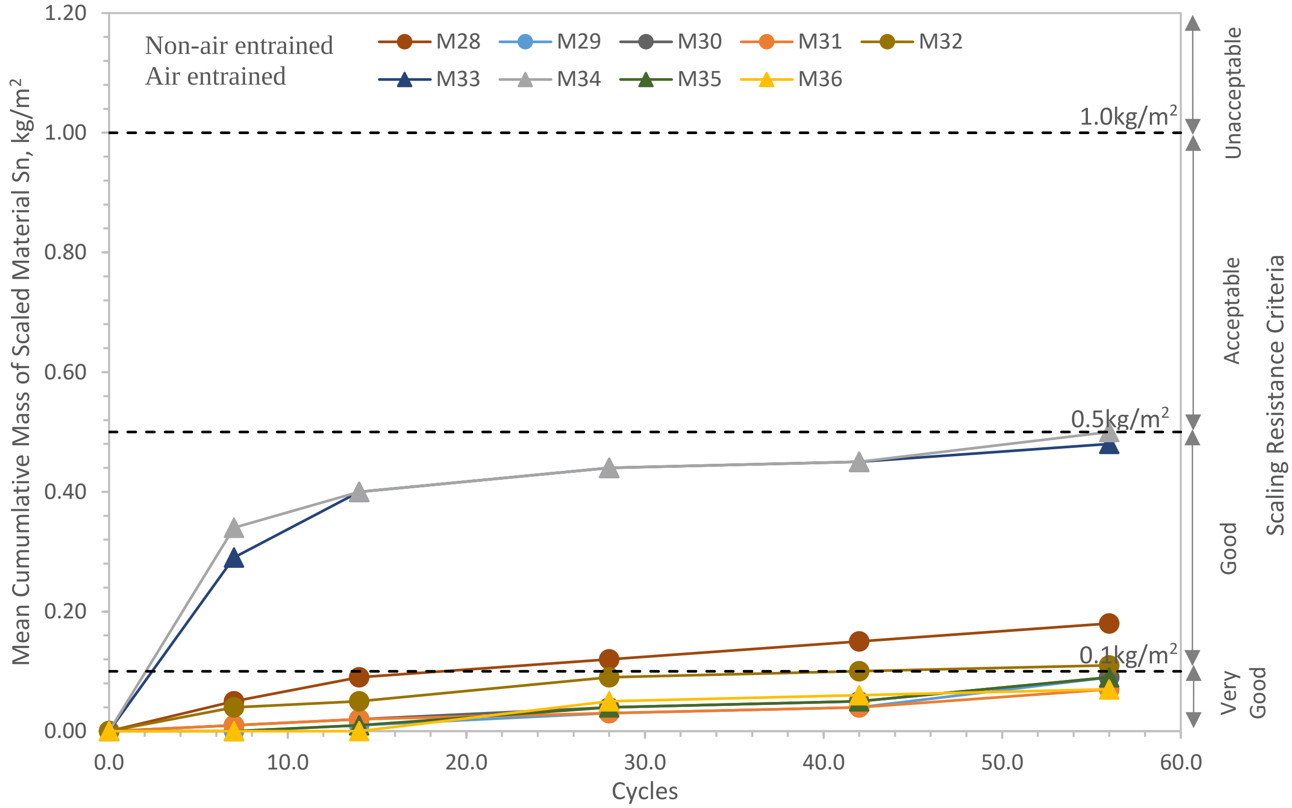


Figure 5.4 Freeze-thaw scaling of CEM III/A Series 1 and 2 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.3 Scaling criteria results for CEM III/A Series 1 and 2 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m²	Approx. Cycle No. of Limit $Sn \geq 1.0 kg/m^2$	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m²/cycle	Confidence Limit, ± kg/m²	[1]Scaling Criteria
	Actual Strength, MPa	w/c	Air Content, %						
Non-Air Entrained (Series 1)									
M28	25.5	0.73	1.0	0.18	na	1.50	0.0594ln(x)	0.18	Good
M29	32.8	0.62	1.0	0.09	na	3.00	0.0368ln(x)	0.21	Very Good
M30	41.1	0.52	1.4	0.09	na	2.25	0.0337ln(x)	0.20	Very Good
M31	51.6	0.45	1.4	0.07	na	2.33	0.0246ln(x)	0.11	Very Good
M32	60.8	0.39	1.4	0.11	na	1.22	0.0361ln(x)	0.09	Good
Air Entrained (Series 2)									
M33	25.5	0.62	4.5	0.48	na	1.09	0.0841ln(x)	0.38	Good
M34	33.8	0.51	4.6	0.50	na	1.14	0.0695ln(x)	0.54	Acceptable
M35	42.2	0.44	4.7	0.09	na	2.25	0.0396ln(x)	0.22	Very Good
M36	51.0	0.39	4.0	0.07	na	1.40	0.0379ln(x)	0.21	Very Good

na – not applicable
[1]In accordance with SS 137244

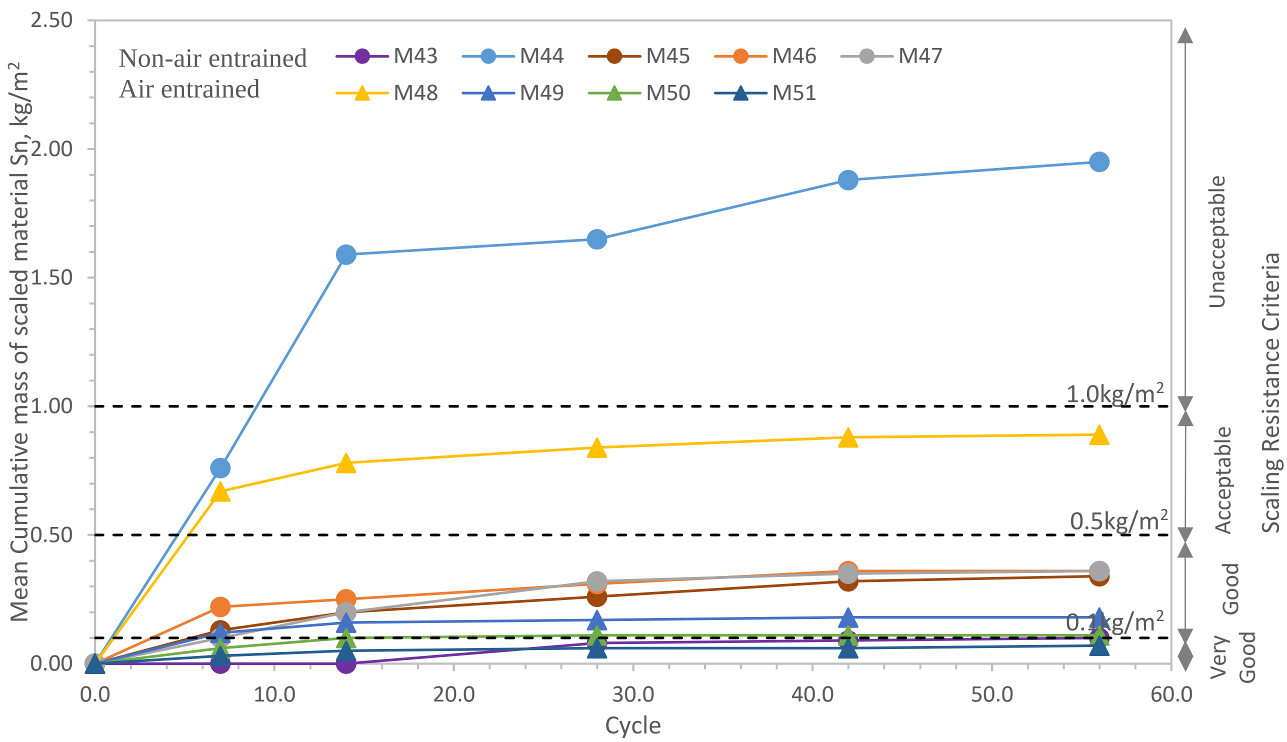


Figure 5.5 Freeze-thaw scaling of CEM II/A-L series 1 and 2 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.4 Scaling criteria results for CEM II/A-L series 1 and 2 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics: Actual Strength, MPa	Mix Characteristics: w/c	Mix Characteristics: Air Content, %	Sn_{56}, kg/m²	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m²	Sn_{56}/Sn_{28}	Rate of Deterioration, kg/m²/cycle	Confidence Limit, ± kg/m²	[1]Scaling Criteria
Non-Air Entrained									
M43	19.8	0.75	1.0	0.10	na	1.25	0.0556ln(x)	0.31	Good
M44	26.3	0.63	1.3	1.95	7 – 14	1.18	0.5234ln(x)	0.44	Unacceptable
M45	36.2	0.54	1.3	0.34	na	1.29	0.1022ln(x)	0.18	Good
M46	48.1	0.46	1.5	0.36	na	1.18	0.0741ln(x)	0.18	Good
M47	59.9	0.4	1.6	0.36	na	1.12	0.1314ln(x)	0.38	Good
Air Entrained									
M48	23.6	0.63	4.4	0.89	na	1.06	0.1053ln(x)	1.24	Acceptable
M49	30.7	0.52	4.3	0.18	na	1.03	0.0278ln(x)	0.19	Good
M50	39.7	0.45	4.4	0.11	na	1.01	0.0226ln(x)	0.07	Good
M51	48.0	0.4	4.5	0.07	na	1.17	0.0174ln(x)	0.01	Very Good

na – not applicable
[1]In accordance with SS 137244

Using the results from Figure 5.1, it is possible to determine the rate of deterioration (kg/m^2/cycle) for each of the mixes using a best fit line allowing for the rate of deterioration equation to be determined. These equations are shown in Table 5.1 along with the total mass of scaled material per square metre (Sn), approximate cycle range where Sn exceeds 1.0 kg/m^2 and the scaling criteria according to SS 137244. Also, in accordance with SS 137244, the values of $^{Sn_{56}}/_{Sn_{28}}$ for each of the mixes that cannot exceed 2.0kg/m^2 for the concrete to be classed as *Acceptable*. This parameter provides problems as its far too generic when used. It is based on the assumption that the scaling of the sample acts linearly providing a straight line when plotted but as results show (Figure 5.1, Figure 5.3 to Figure 5.5) most of the scaling is done in the first 7-14 cycles before levelling off or with a slight increase after each test cycle (7, 14, 28, 42 and 56 cycles).

Using the rate of deterioration, the mass of scaled material can be calculated for a cycle. The rate is determined by finding the logarithmic equation of the line after the test is completed. This equation will permit the user to identify when a concrete approaches the 1.0 kg/m^2 limit if has not reached this value during the freeze-thaw test. Table 5.5 shows a comparison of the rates of deterioration between a non-air and air entrained CEM II-A/L concrete reviewing the mass lost during scaling and the possible mass loss from further scaling.

Table 5.5 Comparison between the rate of deterioration for a non-air and air entrained 30 MPa CEM II/A-L concrete showing how the scaled material loss for each cycle

		Mean cumulative mass of scaled material (Sn), kg/m^2	
		M44 (Non-air entrained)	M49 (Air entrained)
Rate or deterioration, kg/m^2/cycle		0.5234ln(x)	0.0278ln(x)
Cycle no.	7	0.76	0.12
	14	1.59	0.16
	28	1.65	0.17
	42	1.88	0.18
	56	1.95	0.18
	70	2.22	0.12
	84	2.32	0.12
	98	2.40	0.13
	112	2.47	0.13
	500	3.25	0.17

From Table 5.5, based on the results from the freeze-thaw test a rate of deterioration equation can be determined and used to review the mass loss for cycles which could potentially occur. M44 (non-air entrained) has shown to be poor in freeze-thaw but the equation can determine how much scaled material would be lost had the testing continued. After the initial cycles (7 – 14) the rate of deterioration curve begins to steady showing a continual mass loss with testing every 14 cycles. From cycle 42 onwards the amount of scaling decreases meaning that the total mass loss is reaching a plateau point where the amount of scaling is very small. Table 5.5 also shows a scaling mass loss for cycle 500 showing that the equation can predict scaling values for the n^{th} cycle. It can be implied that as less scaling has occurred as the poorer concrete layer is now removed, leaving the bulk concrete exposed and able to resist freeze-thaw attack.

Similarly, the air entrained concrete can be predicted once the initial 56 cycles have been tested then an equation developed to determine when the scaling limit is reached. For M49 the amount of scaled material is small meaning theoretically it would take a very long time for the concrete to reach the Unacceptable rating as shown by the difference between cycle 112 and 500. The freeze-thaw data has shown that for a high rate of deterioration results in a high total mass of scaled material. M44 has a high rate and a high Sn value (at 56 cycles) whereas for M49 it has a low rate and low Sn value.

Though a rate of deterioration can be determined using the test results, the rate cannot be calculated prematurely. The rate is based on the collective of data up to 56 cycles (the duration of the freeze-thaw test) as it requires the stabilization of the material loss meaning that the loss of material is required to reach a point where the loss is linear in order for the calculation to be done, for example, the rate cannot be determined until after 28^{th} cycle otherwise the rate equation would change in gradient assuming the rate will continually lose material as seen in the first 7 cycles of the freeze-thaw test.

5.2.1 The Effect of Using CEM II/B-V Concretes in Freeze-Thaw Conditions

Figure 5.3 depicts air and non-air entrained CEM II/B-V concretes for various target strengths and

Table 5.2 gives the values for Sn after 56 cycles and rate of deterioration for each of the mixes. Similarly, to M1, since M13 has such a low strength of 20 MPa, but when tested for freeze-thaw durability, the concrete has an *Acceptable* outcome. This relates to the low strength of the concrete and the poor outer surface of the concrete wear continual freezing and thawing causes the silicon sealant to contract and expand respectively pulling on the concrete. The saline solution poured on top for testing then leaks down the sides of the sample, stopping any further scaling of the surface, thus, reducing/stopping any deterioration of the concrete giving it an *Acceptable* rating.

Due to the nature CEM II/B-V concretes whereby the fly ash material is variable in regard to its physical characteristics it is difficult to pinpoint when the samples are going to pass the 1.0kg/m^2 mark to become

Unacceptable during freeze-thaw. Aside from M13, all the non-air entrained concretes (M14 – M17) all surpass the acceptable band (1.0kg/m^2) for freeze-thaw including M17 that had a 28-day strength of 60.0 MPa. Furthermore, M17 did not become an 'unacceptable' concrete near the end of the test but rather before the midpoint (see Table 5.2). This illustrates that even with a high strength concrete CEM II/B-V concretes are unable to provide acceptable durability during freeze-thaw performance. Mixes M18 – M21 show a very good freeze-thaw resistance with the inclusion of air entrainer. M18 is observed to have an *Acceptable* Sn value of 0.55kg/m^2 which can be attributed to the lower strength of 20 MPa, though it should be noted that with the inclusion of air entrainment, the lower strength concretes such as 20 MPA and 30 MPa did not see the outer concrete layer detach from with the silicon sealant. It can be considered that with the added air entrainment, the poorer outer layer retains some strength during the freeze-thaw cycles allowing the infiltration of water and freezing to occur without damaging the concrete.

5.2.2 Performance Comparison Between CEM I and CEM II/B-V Concretes

Comparing CEM I to CEM II/B-V concretes (Figure 5.6 and Figure 5.7) shows a distinction between both the concrete's durability to freeze-thaw resistance. For non-air entrained CEM I concrete there is a trend between the strength and the mass loss from scaling. Increasing the strength will reduce the mass loss during freeze-thaw though the same cannot be said for CEM II/B-V. Even with the increased strength, the concrete still does not meet acceptable criteria for freeze-thaw showing that even with the increase in the strength, it does not provide enough protection for freeze-thaw. As with M1, M13 is deemed to be an outlier as it has had the same issue with the silicon sealant peeling away from the sample allowing the saline solution to dissipate down the sides reducing the rate of deterioration, thus, giving an inaccurate value for the scaled mass loss.

There is no correlation between the strength and freeze-thaw durability for CEM II/B-V. M15 (40 MPa) performs slightly better than M17 (60 MPa) confirming that even the fly ash from the same batch provides different results, therefore, can be unpredictable. It is understood that concrete containing fly ash is known to take longer for the pozzolanic reactions to occur (approximately 56 days after casting (Wang & Park, 2015).

With the delayed reaction time of the fly ash, there is a sudden increase in the mass loss due to scaling, then even with the increase in the strength (Figure 5.3) continuous mass was still lost to scaling. Moreover, when the pozzolanic reactions do occur it also becomes a hindrance to the concrete's durability. During the reactions, the voids in the cement paste are filled with hydration products between the cement and fly ash reducing the volume of void space inside the paste matrix.

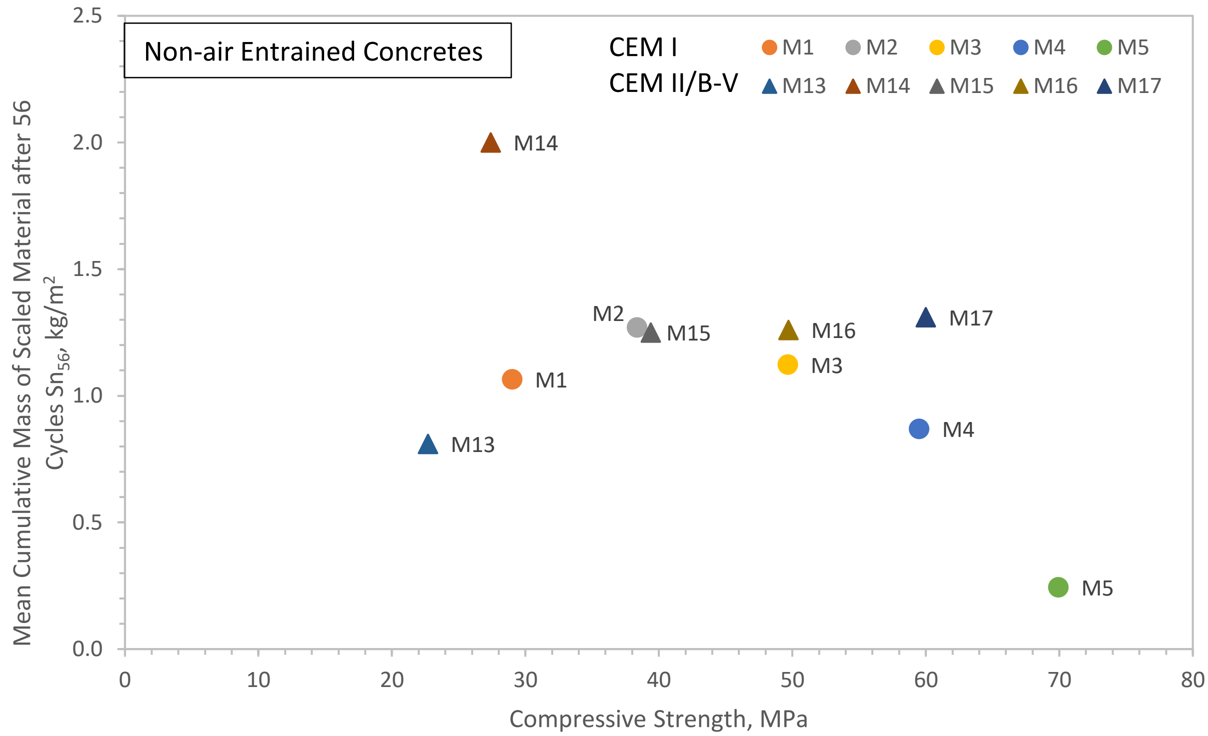


Figure 5.6 Comparison between non-air entrained CEM I and CEM II/B-V concretes for both compressive strength and total mean cumulative mass of scaled material

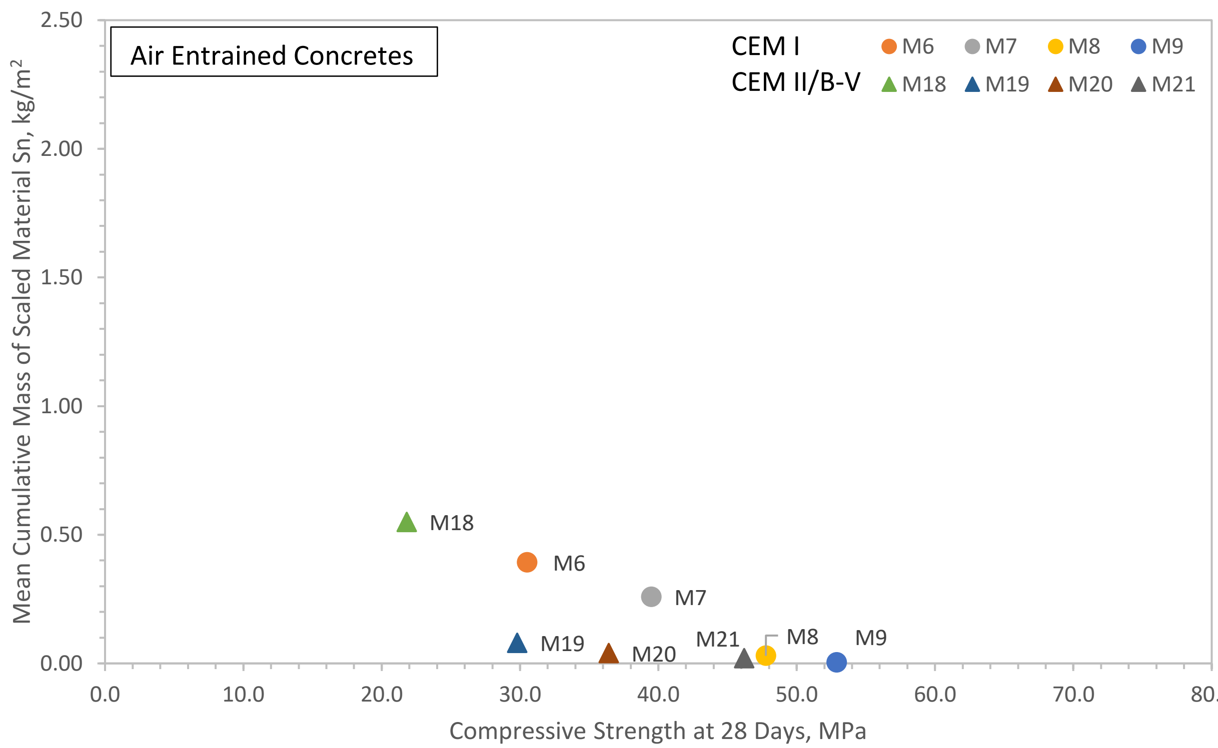


Figure 5.7 Comparison between air entrained CEM I and CEM II/B-V concretes for both compressive strength and total mean cumulative mass of scaled material

The benefit of this is that with these reactions taking place there is densification of the concrete improving its strength. However, the reduced void space inside the concrete means there is little room for the saline solution to expand into during the freezing process once it has infiltrated the surface. The reduction in space leads to significant cracking from the expansion of ice in the saturated voids.

Given that the delayed reaction time for the fly ash, a hypothesis considered by the author about why the concrete containing fly ash has an increase in strength but also an increase in the mass loss during freeze-thaw scaling:

'The densification of the concrete containing fly ash replacement increases the strength of the sample but is also compromises its freeze-thaw resistance by reducing void space, which in turn, reduces capacity for the ice to expand leading to cracking and eventual mass loss.'

The longer duration for the pozzolanic reactions to take place there is some scaling taking place during the first 7 cycles. Afterwards, a significant amount of scaling is seen (cycles 7 – 14, Figure 5.3) before tailing off. This refers to the hypothesis that the delayed reaction time of the fly ash means that initial scaling will occur then once the densification does take place by then it is too late as the damage has already weaken the concrete's structure. So even though significant mass loss has already occurred, and the mass loss is plateauing, there is still some material continuing to scale off.

CEM I illustrates a steady decrease in the mass loss with every 10 MPa increase in compressive strength resulting in zero mass loss for a 50 MPa strength air entrained concrete. Similarly, CEM II/B-V concretes show a decrease in mass loss with increase in the strength. Despite the inclusion of air entrainment in the concrete there is still scaling for CEM II/B-V concretes. This can be related to the low compressive strength. Nonetheless, the concrete performs 'acceptably' well with the mass loss equating to 0.55kg/m^2.

5.2.3 The Effect of Using CEM III/A Concretes in Freeze-Thaw Conditions

Concrete containing GGBS (ground granulated blastfurnance slag) has been identified to cause problems in relation to the air void system and freeze-thaw resistance (Wawrzenczyk, et al., 2016). Figure 5.4 illustrates the freeze-thaw performance of CEM III/A Series 1 (non-air entrained) and 2 (air entrained) concretes designed with varying target strengths.

As shown in Figure 5.4, both the air and non-air entrained concretes performed very well during freeze thaw with the total mass loss for all the concretes remaining under 0.5kg/m^2. Previous work has looked at the effects of air entrainer in CEM III/A concrete and it shown to have no effect despite the target air content for the concretes achieving 4.5%. Moreover, M33 (20 MPa) and M34 (30 MPa), both air entrained, showed poorest performance within the series losing 0.5kg/m^2 each which is considerably more than the non-air entrained equivalent M28 (20 MPa) which only lost 0.18kg/m^2.

On the other hand, CEM III/A concrete is susceptible to curing issues due to the slower rate of hydration compared to CEM I. Overall, from the results shown in Figure 5.4 and Table 5.3, the concrete containing air entrainment were outperformed by their non-air entrained counterparts showing that the inclusion of air entrainment into a GGBS concrete causes it to perform worse than non-air entrained.

5.2.4 Performance Comparison Between CEM I and CEM III/A Concretes

Comparing the strengths and mass loss for CEM I and CEM III/A Series 1 shown in Figure 5.21 Freeze-thaw scaling of CEM II/B-V, CEM III/A and CEM II/A-L Series 4 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.8, the chart illustrates very similar results between the cement types. The strengths all either match or surpass their respective target strength though there are differences between the freeze-thaw scaling. CEM I initially has high scaling with the lower strengths, decreasing as the compressive strength increases. However, CEM III/A there were minor scaling even with the 20 MPa strength which then continues to reduce until M32 (60 MPa) where the scaling loss increases slightly. This can be similar to what was seen in the CEM II/B-V concretes where with the slow rate of hydration, the compressive strength does not reach its peak in time resulting in early freeze-thaw scaling.

This leads to the possibility that if a CEM III/A concrete is used in freeze-thaw conditions without air entrainer then a 60 MPa strength is enough to reduce or prevent deterioration. Otherwise if an air entrainer is then used in order to match the durability of its non-air entrained counterpart then it would need a 50 MPa strength following the results from Table 5.3.

Figure 5.9 shows the compressive strength and the total mass loss for CEM I and CEM III/A air entrained concretes. Unlike Series 1, there are no similarities between scaling results. As shown, CEM III/A concretes do not perform better with air entrainer and in fact air entrainer (though provides an air entrained microstructure) is inert from a durability aspect and potentially hinders the scaling resistance particularly with lower strength concretes as shown in Figure 5.9.

5.2.5 The Effect of Using CEM II/A-L Concretes in Freeze-Thaw Conditions

Figure 5.5 and Table 4.4 detail the results for CEM II/A-L series 1 and 2 illustrating the loss of material through 56 cycles and the rate of deterioration.

As the results show only one sample did not achieve an *Acceptable* rating which relates to the strength of the concrete. Moreover, it was observed that despite M43 being a lower strength (20 MPa) than M44 (30 MPa) it was still capable of achieving a very good scaling rating compared to M44 which did not reach an acceptable rating. This is linked to the weakness of the concrete whereby during the freezing and thawing process the concrete is cracking quickly, and the saline solution is leaking out preventing freeze-thaw scaling to occur on the surface. This manipulates the results into an ideal that the concrete performs well during the test but, full freeze-thaw cycling cannot occur because of continual surface cracking.

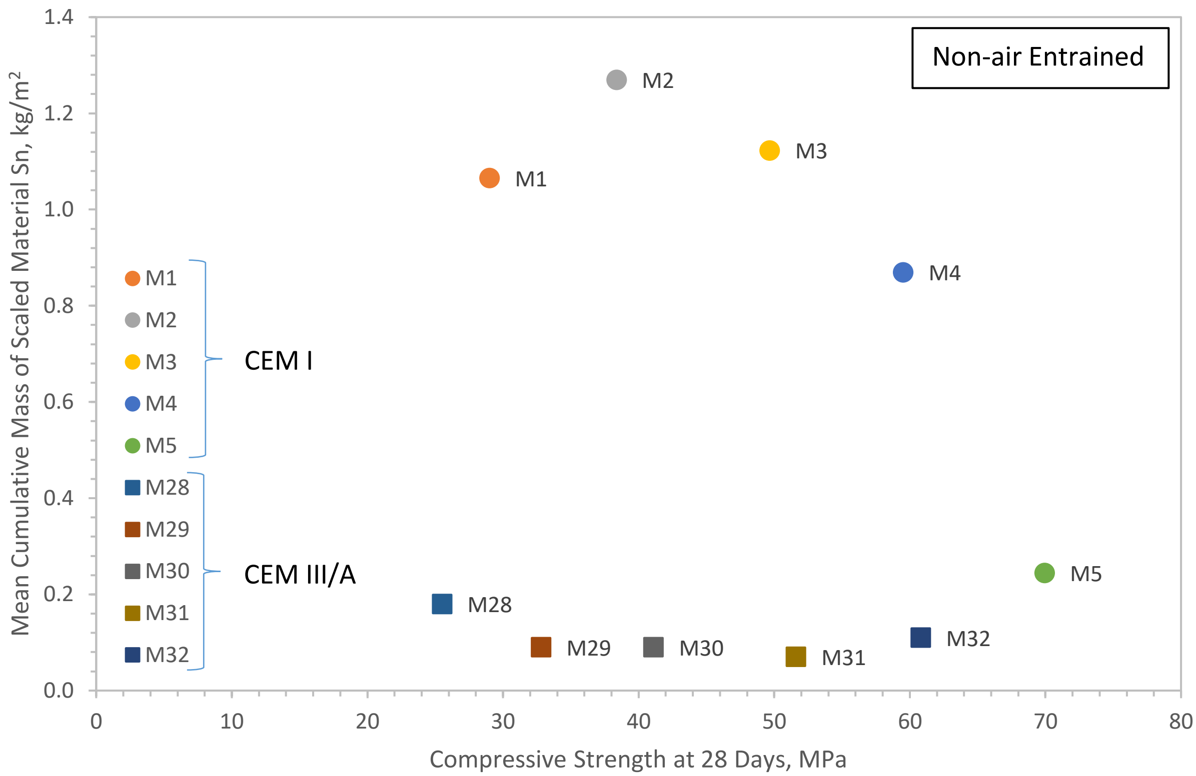


Figure 5.8 Comparison between CEM I and CEM III/A Series 1 concretes for both compressive strength and total mean cumulative mass of scaled material

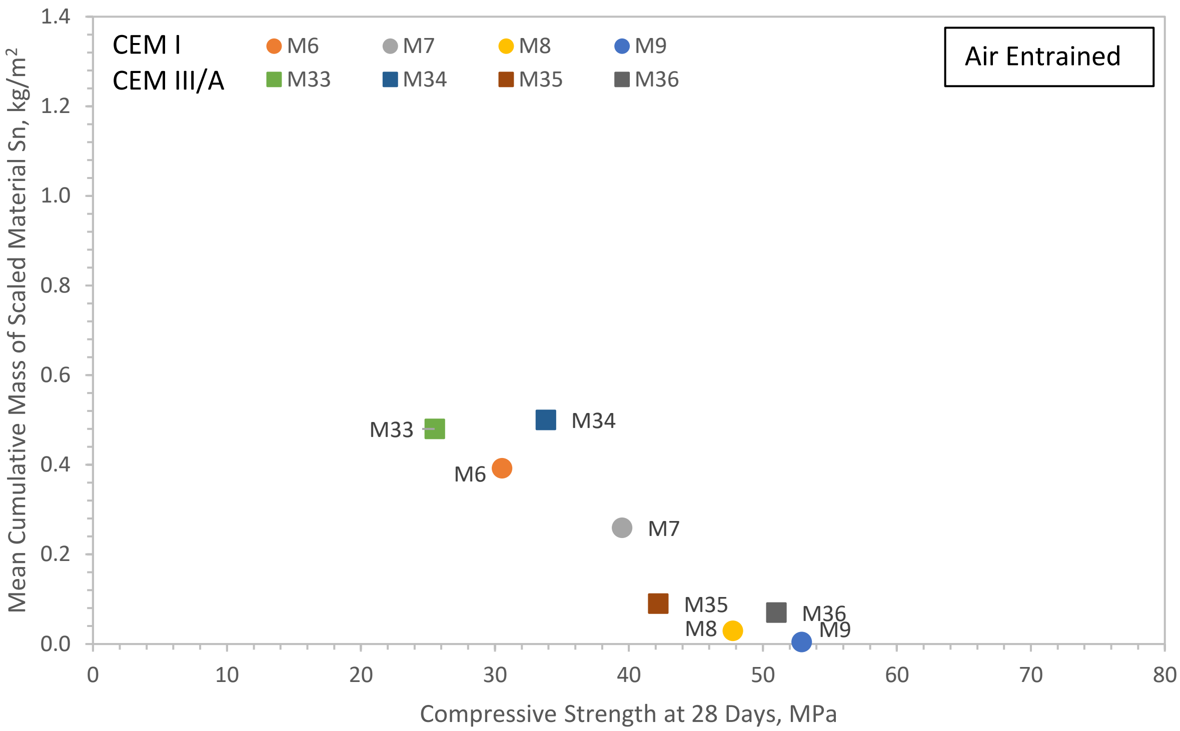
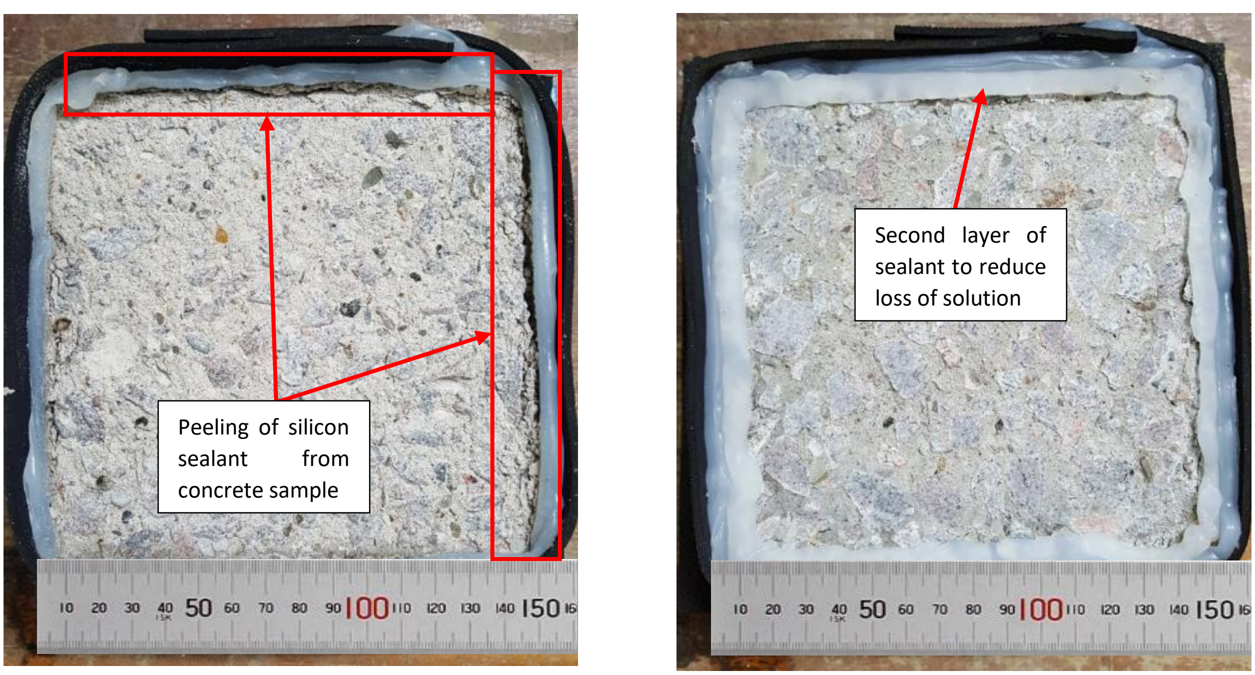


Figure 5.9 Comparison between CEM I and CEM III/A Series 2 concretes for both compressive strength and total mean cumulative mass of scaled material

Furthermore, and seen in other concretes, it is the effects of cracking on the concrete surface which influences the freeze-thaw scaling results. M43 saw cracking around the edges with small pieces breaking off during the test (Figure 5.10). The cracking (whether it be internally or externally) is then impinging the



results whereby the freeze-thaw cannot take place on the concrete resulting in the sample achieving a very good scaling rating.

Figure 5.10 CEM II/A-L non-air entrained concrete showing (a) cracking and loosening around the edges of the samples as it is pulled away by the silicon sealant and, (b) the solution to rectify the loosening of the sealant is by additional sealant around the edge when required

5.2.6 Performance Comparison Between CEM I and CEM II/A-L Concretes

Limestone is an inert material meaning that it has no influence over the chemical properties in the concrete like fly ash or GGBS. However, even with the material being chemically inert, the concrete's performance in freeze-thaw is shown to perform better in freeze-thaw than CEM I. Figure 5.11 shows the comparison between the compressive strength and the freeze-thaw scaling results for the non-air entrained CEM I and CEM II/A-L concretes whilst Figure 5.12 shows the same comparison for the air entrained concretes.

The comparisons show that without air entrainment, the CEM I concrete which had lower strength (less than 50 MPa), did not have the ability to withstand freeze-thaw attack. On the other hand, apart from M44, all the other CEM II/A-L concretes achieved good scaling resistance rating. Though the result for M43 seems to provide a false *Good* rating because of the lower strength of the concrete. This stems from the issue of the silicon peeling of the sample and removing concrete allowing the solution to leak down the sides. As stated M44 did not achieve an acceptable scaling rating in accordance with SS 137244 even with

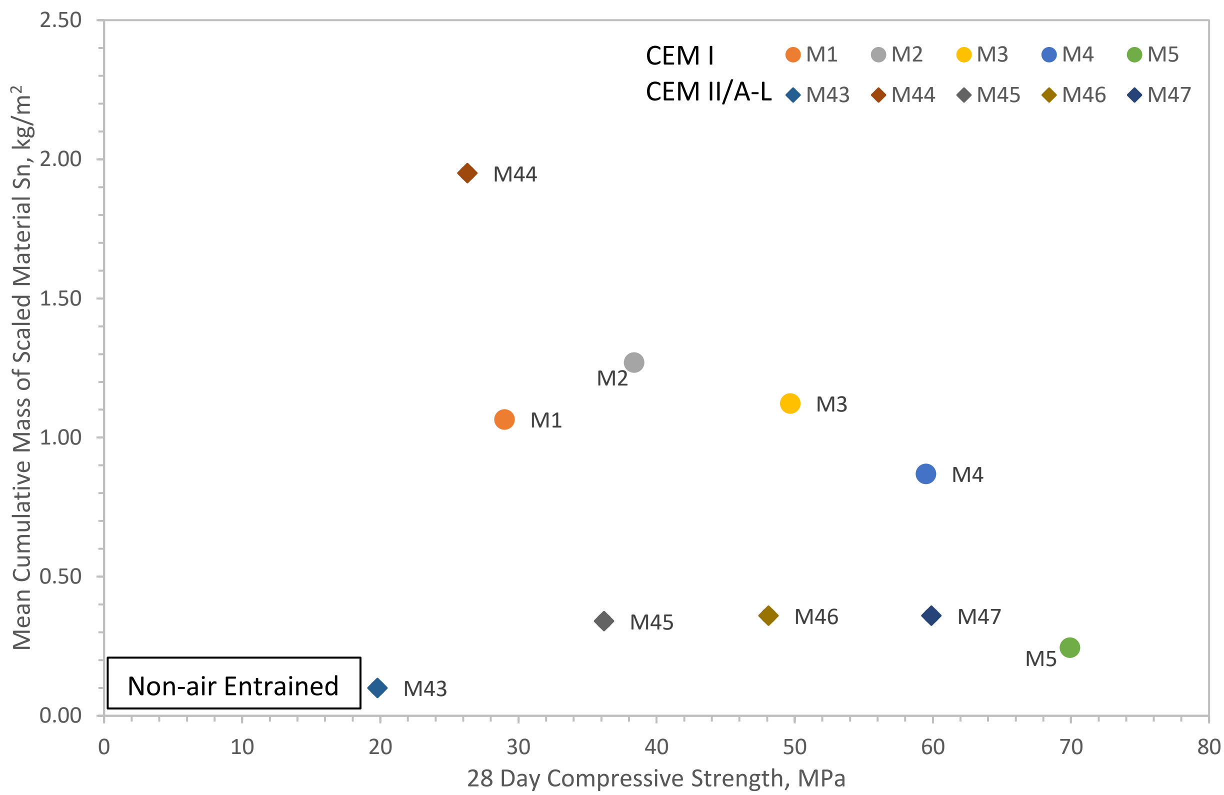


Figure 5.11 Comparison between non air entrained CEM I and CEM II/A-L concretes for both compressive strength and total mean cumulative mass of scaled material

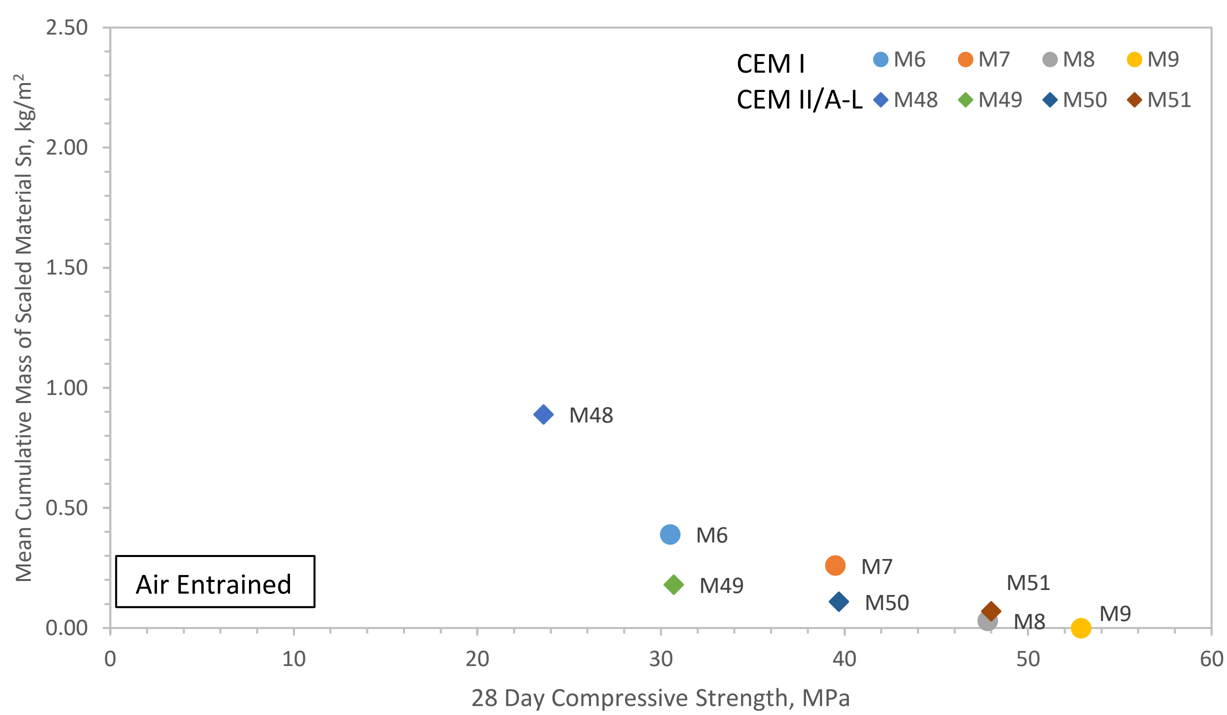


Figure 5.12 Comparison between non air entrained CEM I and CEM II/A-L concretes for both compressive strength and total mean cumulative mass of scaled material

a moderate design strength of 30 MPa, whereas, M43 which has a design strength of 20 MPa managed to achieve a very good rating. This rating is the result of small sections of the concrete breaking from the main sample allowing the water to leak down the side preventing full freezing and thawing to take place as the sample was resealed and testing continued only for the same issue to arise.

Furthermore, the number of concretes which have been able to withstand freezing and thawing was higher for CEM II/A-L than CEM I. As previously discussed, limestone particles are smaller than standard CEM I particles with the mean particle size for limestone is 5.9μm and 15.9μm for CEM I showing that the average particle size is smaller for limestone suggesting that more particles could be densely packed together between the CEM I particles reducing the volume of air voids within the concrete, thus, decreasing the amount of solution capable of infiltrating into the concrete's voids and freezing (Sajedi & Shafigh, 2012).

Furthermore, the D_{10} particles size for CEM I and limestone are 3.1μm and 1.4μm respectively showing that for 10% of the particle size for limestone is smaller. Similarly, for D90, the sizes are 44.5μm and 19.6μm respectively stating that overall, when CEM II/A-L cement is used then it has better freeze-thaw resistance due to the reduced void space in the concrete.

Even though CEM II/A-L does not have the same durability rating as CEM I, there is still a clear trend in the results. All the concretes show a similar trend where the increase in the strength reduces the amount of scaled material. This observation identifies that even with a material which was previously classified as a filler and not a cement replacement and does not react with CEM I during the hydration process, still shows promise that it can be used in a concrete subjected to freeze-thaw with minimal strength loss with or without air entrainer.

5.3 Influence of Air Void Parameters on the Scaling of Non-air and Air Entrained Concretes with Different Cement Types (Series 1 and 2)

Freeze-thaw resistance of concrete had always been determined based on Powers spacing factor as a method of identifying the durability of concrete. Initially when the spacing factor value was first implemented for freeze-thaw analysis, concrete was solely based on using CEM I. Recently, with new sustainability directives from the EU and the development of cement types and new admixtures, this means that using the spacing factor parameter by itself is not enough to determine how the concrete would perform during freeze-thaw.

Recently new technology has been introduced as a means of determining the microstructure of the concrete, thus, providing data to foresee (approximately) how well a concrete would resist freeze-thaw or if it has the potential to not achieve an acceptable scaling rating. Chapter 4 looked at the various air void parameters such as spacing factor, specific surface and void frequency and the correlation between air contents of fresh and hardened concretes.

Figure 5.1,Figure 5.3 to Figure 5.5 show the scaling data of different cement types at different strengths for both air and non-air entrained after 56 cycles against a number of air void parameters which were calculated by the air void analyser using the equations detailed in BS EN 480-11. This suggests that using one air void characteristic as a comparison does not illustrate a concretes performance clearly enough to determine whether a concrete would be able to withstand freeze-thaw.

Figure 5.13 shows the results for CEM I in comparison to the different air void parameters. The data shows minimal correlation between the parameters when the air and non-air entrained samples are compared regarding the scaling data. Whilst there is a clear separation between the air and non-air entrained concretes, there is no visible trend in the results. The distribution between the small 'groups', non-air and air entrained, provide less comparable data for certain characteristics. Looking at only the scaled material loss there is a direct relationship between the increased strength and the loss of scaled material (Figure 5.8 and Figure 5.9). However, comparing concretes using air void parameters shows little correlation between them.

In the previous Chapter, it was discussed that using spacing factor as the primary air void parameter was not suitable to provide a good approximation of the freeze-thaw durability because of its inability to deviate from averaging the results to determine a single value. It was then considered to utilise other air void characteristics instead which could then be used simultaneously in order to determine a *'collaborative agreement'* on the suitability for a concrete to be used in freeze-thaw conditions (Hasholt, 2014).

On the other hand, if the air void characteristics are plotted against the scaled material it becomes difficult to determine how a concrete would perform. It was discussed that using air content, specific surface and void frequency would be a better choice compared to using the spacing factor only. However, in this instance using the specific surface does not provide clear distinction as to whether a concrete is suitable when compared to freeze-thaw data. According to Neville (1995), the specific surface for an air entrained concrete should be higher than the specific surface of a non-air entrained concrete. This statement is the general consensus detailing that the more air there is in the concrete the more specific surface (total void space) as detailed in the following equation:

$$Specific\ Surface\ mm^{-1} = \frac{Totat\ surface\ area\ of\ air\ voids\ mm^2}{Total\ volume\ of\ air\ mm^3}$$

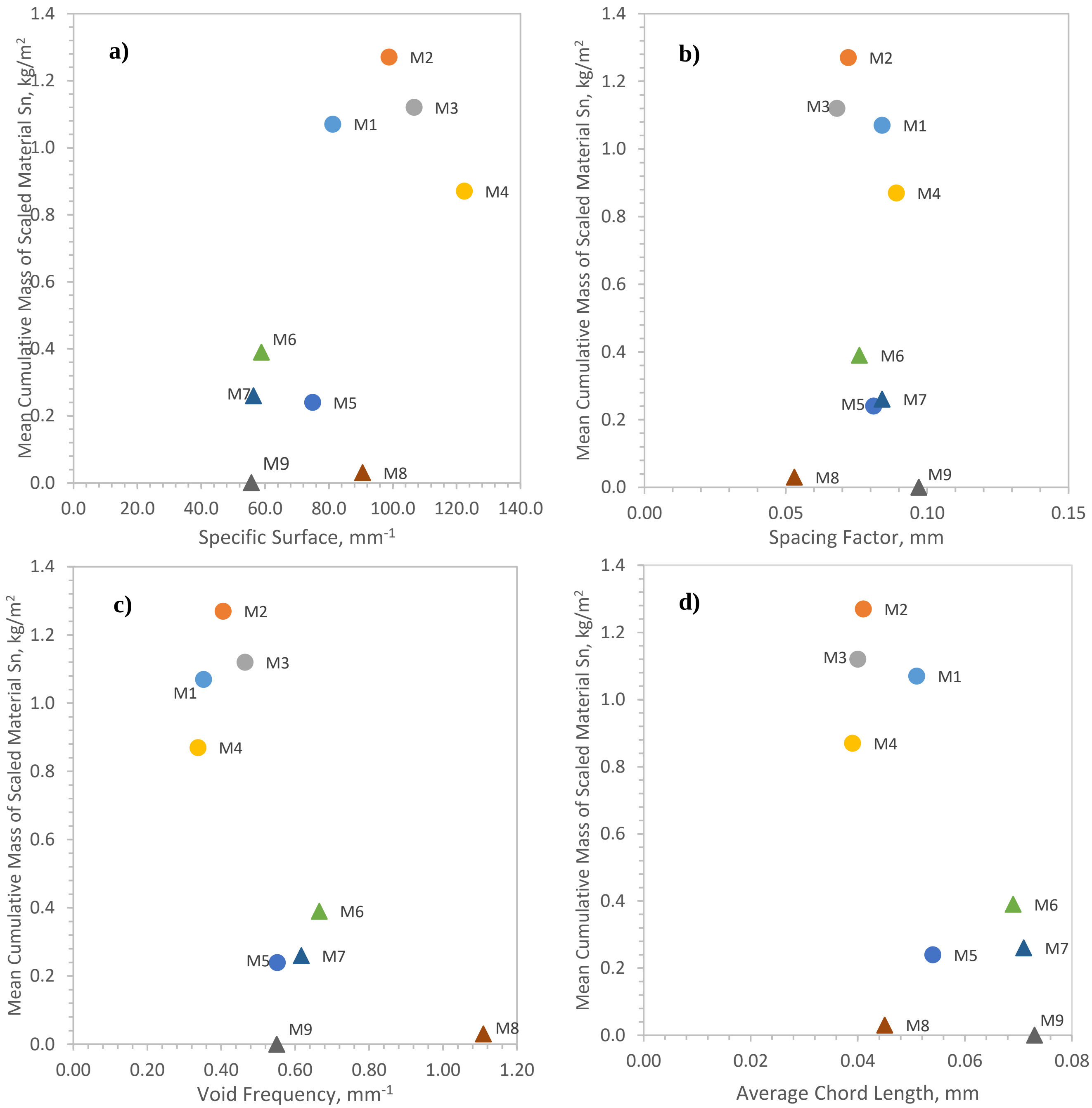


Figure 5.13 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of CEM I non-air and air entrained concretes after 56 cycles (Series 1 & 2)

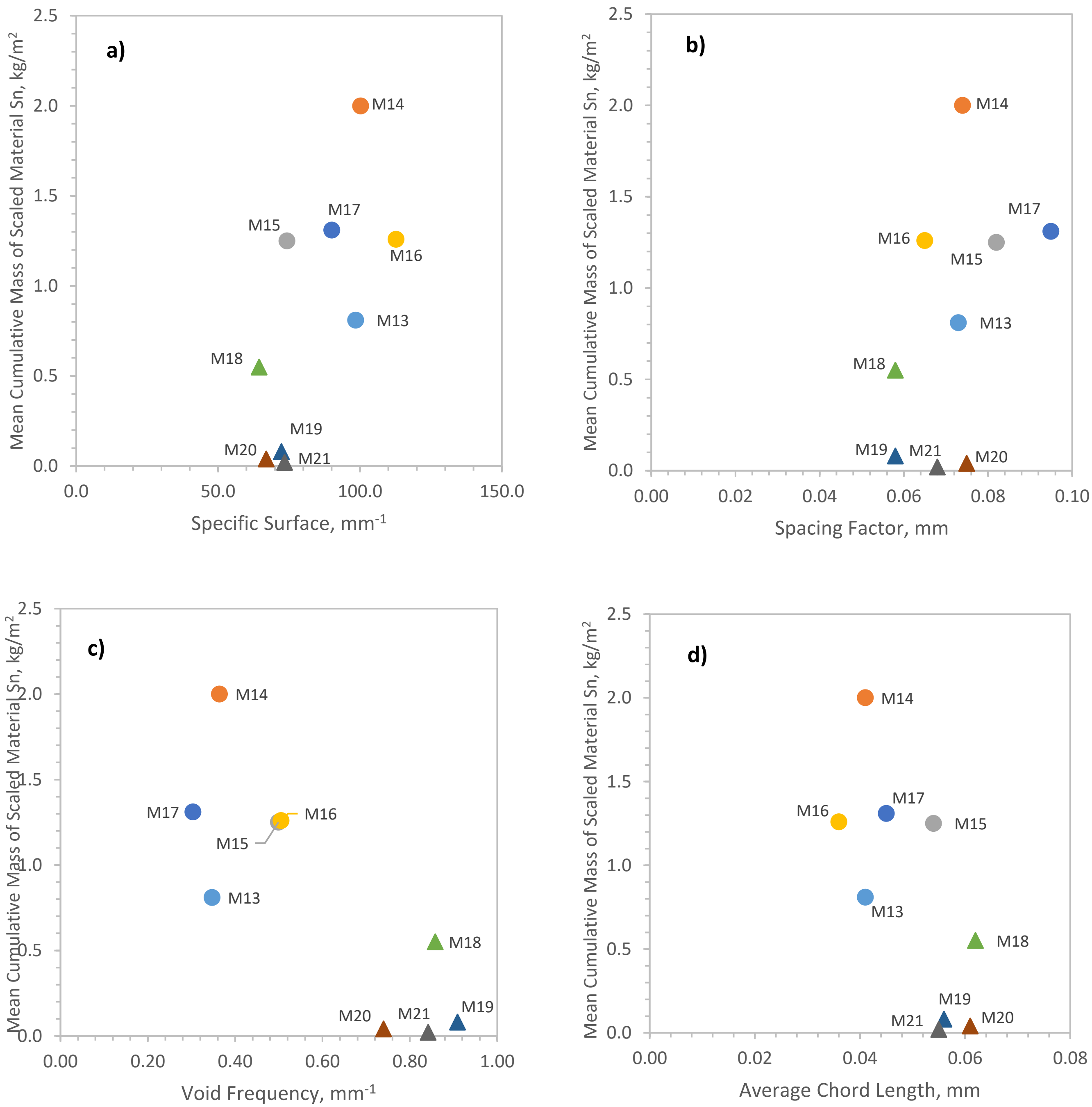


Figure 5.14 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of CEM II/B-V non-air and air entrained concretes after 56 (Series 1 & 2)

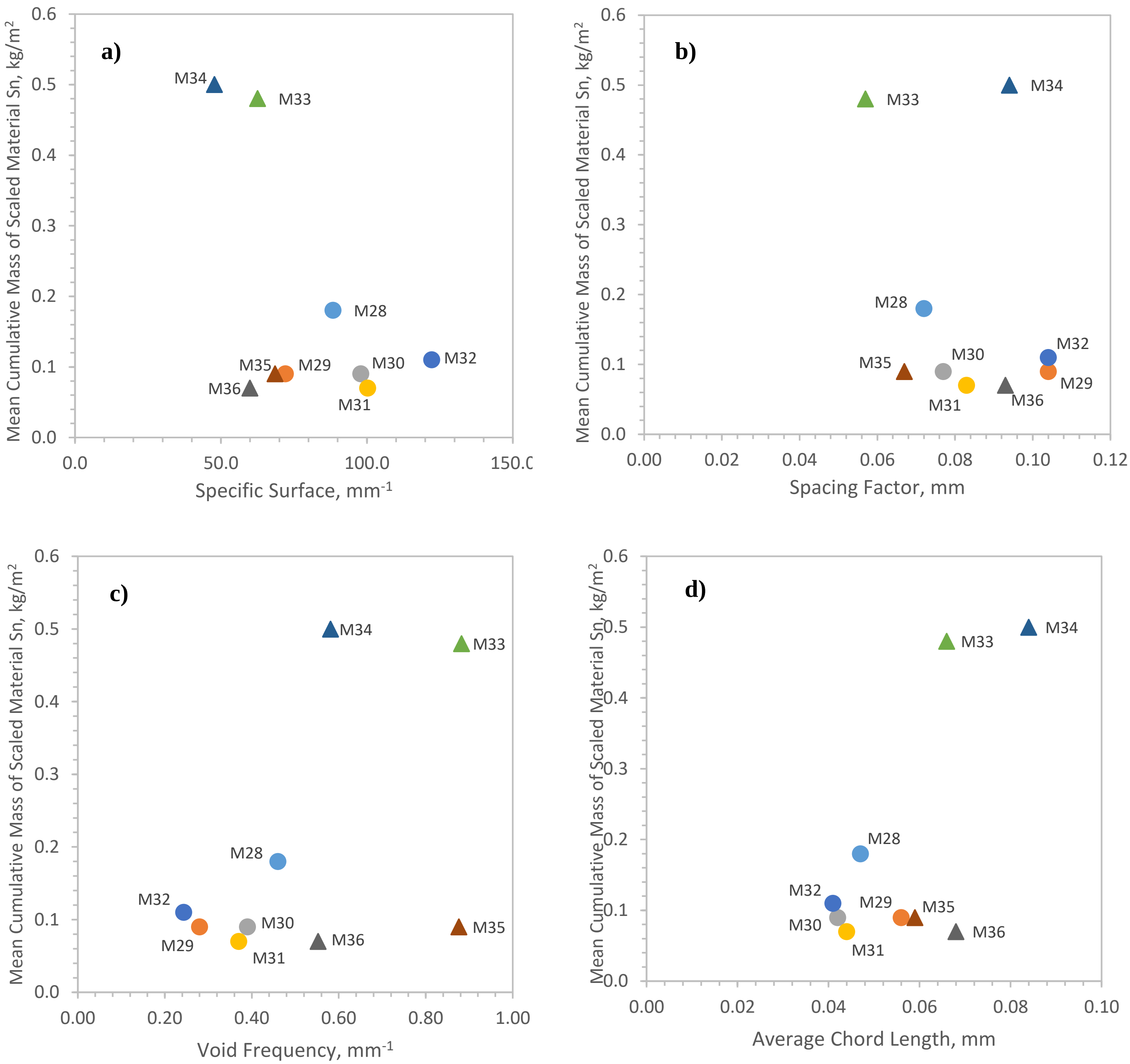


Figure 5.15 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of CEM III/A non-air and air entrained concretes after 56 cycles (Series 1 & 2)

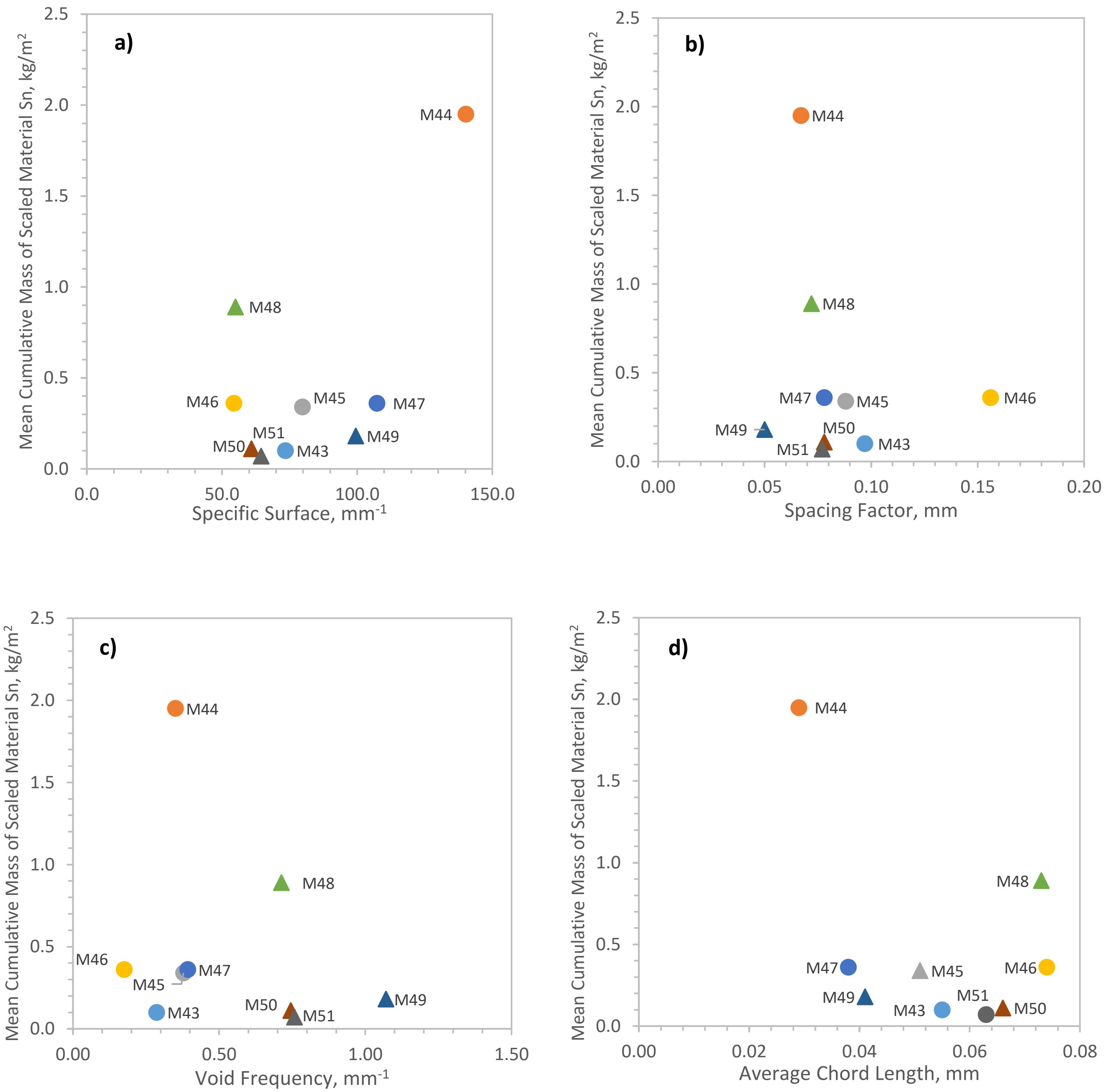


Figure 5.16 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of CEM II/A-L non-air and air entrained concretes after 56 (Series 1 & 2)

In reality the above statement is difficult to prove with the results shown in Figure 5.13 to Figure 5.16. As the results show CEM I and CEM II/B-V non-air entrained concretes have a higher specific surface than the non-air entrained, however, for CEM III/A and CEM II/A-L have the higher specific surface values for the air entrained concretes. Using specific surface would prove some correlation between the air void parameter and the scaling data but the results are not accurate enough to provide a definitive answer as to whether a concrete would have good enough durability for freeze-thaw.

Comparing the scaling results to the spacing factor results, there is very little correlation between these results for all the concretes. This relates to the microair voids produced using admixtures. Admixtures used today are developed in such a way they have other secondary qualities. This includes superplasticizer which has a secondary benefit of being an air entrainer. Although, regarding freeze-thaw resistance, this a very good benefit it does in fact affect the outcome of the spacing factor result. Whilst the superplasticizer does increase the workability it also increases the possibility of air being entrained.

From the analysis that was carried out in Chapter 4, the data shows a small amount of air was being entrained into the concrete by the superplasticizer. Although the air content was low (approximately 1.2% or less) it did affect the microair content. Microair is the total air content of void sizes 300µm or less, and it was found that the smallest of void sizes (measuring 10-30µm) were equal for both air and non-air entrained concretes. This meant that when the calculation for the spacing factor was completed the values were approximately the same because of the dispersion of the air voids throughout the sample, and the spacing factor is determined by the average space between each of the voids.

The influence of the microair on the spacing factor can be seen in Figure 5.13b to Figure 5.16b whereby the data points create a column where the air entrained concretes are at the bottom and the non-air entrained samples are at the top. If the spacing factors followed the definition outlined by Powers, then the results would show non-air entrained samples would have a spacing factor larger than 250µm and an adequately air entrained concrete would have a spacing factor less than 100µm. The theory is partly accurate as all the air entrained samples do have a spacing factor less than 100µm.

Average chord length is another parameter which does not provide a suitable correlation with freeze-thaw scaling. The average chord length is defined as the average void size within the concrete microstructure and as with the spacing factor, it is hard to determine the true value of the parameter because of the side benefits of current admixtures. Aforementioned, it is better to have smaller, evenly distributed voids of the same size throughout the concrete rather than having a small amount of large voids, although if no air entrainer was used in the concrete then the average chord length should be large based on the premise that there was a small amount of entrapped air. Again, the parameter is affected by the side benefits of new superplasticizers.

Considering the average chord length graphs (Figure 5.13 to Figure 5.16 (part d)), whereby the average chord lengths show the non-air entrained concretes to be smaller than air entrained. It can be construed that because there are less voids in total for non-air entrained concretes that the results are misleading compared to the air entrained counterparts. However, because there are less smaller voids the average chord length would then be affected by the entrapped air voids which have a larger diameter, hence, a higher average chord length. Moreover, applying the same theory to air entrained samples would not have as much of an affect because there a more voids in total so if there is the odd large entrapped void then the offset would not be as noticeable.

Out of the air void parameters, void frequency is the preferred parameter when comparing to freeze-thaw scaling. From the above figures there is a clear correlation for the void frequency which better shows how the scaling relates to the microstructure of the concrete. Void frequency is determined by the total number of voids which are counted divided by the length of the traverse. In theory, the more voids which are interacted by the analyser over the traverse length the higher the void frequency. From the results previous this statement is seen to be true. Apart from a few outliers, the distributions for each of the cement types detail that the non-air entrained concretes have a lower void frequency whilst having a high scaling value shown in Tables (Table 4.1 to Table 4.4 in Chapter 4 showing air void characteristics).

5.4 Freeze-Thaw Scaling of Concretes with Varied Target Air Contents (Series 3)

5.4.1 Influence of Varying the Air Contents on the Freeze-Thaw Scaling Resistance of Concrete

Series 3 of the concrete mixes were designed to have an increase in air content to determine if there was an upper limit where too much air entrainment would benefit/hinder the freeze-thaw performance. Different cement types were used along with increasing the air content in 2.5 % intervals (starting at 4.5 % then 7 %, 9.5 % and 12 %) and the samples were tested for freeze-thaw. Figure 5.17 and Figure 5.18 show the freeze-thaw scaling results for all the concretes with different air contents and Table 5.6 and Table 5.7 show the mix characteristics and results for each of the mixes.

As seen in the Figure 5.17, all mixes have a scaling resistance classed as very good according to SS 137244 with none of the mixes losing nothing more than 0.1 kg/m^2. All the concretes in this casting series had a target strength of 40 MPa. Despite the increase in the air entrainment, CEM I concrete still managed to achieve the target strength and only being slight differences between the mixes when compared to one another. Moreover, when these results are compared to the non-air entrained CEM I concrete with a higher strength, it is shown that the concrete does not perform as well as the air entrained.

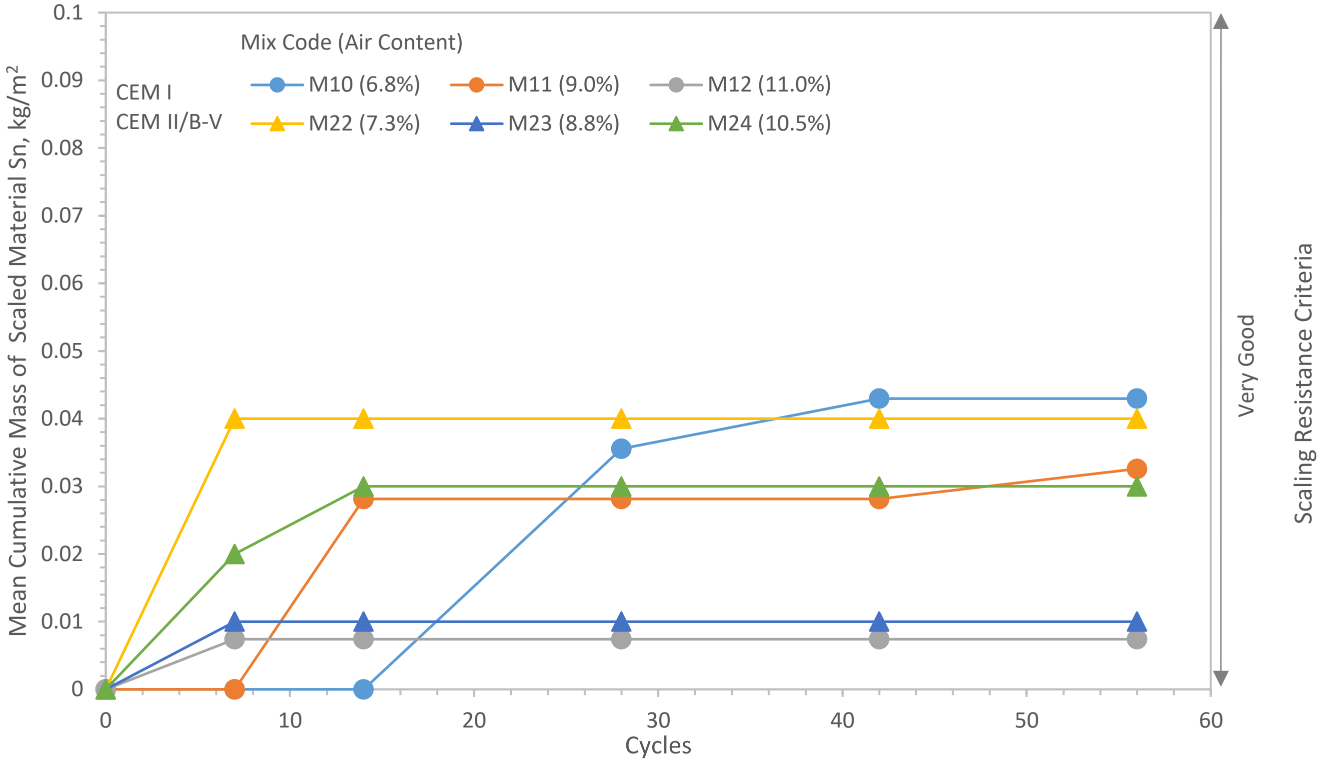


Figure 5.17 Freeze-thaw scaling of CEM I and CEM II/B-V Series 3 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.6 Scaling criteria results for 40 MPa strength CEM I and CEM II/B-V Series 3 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m^2/cycle	[1]Scaling Criteria
	Concrete Type	w/c	Air Content, %					
M10	CEM I	0.45	6.8	0.04	na	1.21	0.0249ln(x)	Very Good
M11	CEM I	0.45	9.0	0.03	na	1.16	0.0131ln(x)	Very Good
M12	CEM I	0.45	11.0	0.01	na	1.00	0.0074	Very Good
M22	CEM II/B-V	0.4	7.3	0.04	na	1.00	0.04	Very Good
M23	CEM II/B-V	0.4	8.8	0.01	na	1.00	0.01	Very Good
M24	CEM II/B-V	0.4	10.5	0.03	na	1.00	0.0042ln(x)	Very Good

na – not applicable
[1]In accordance with SS 137244

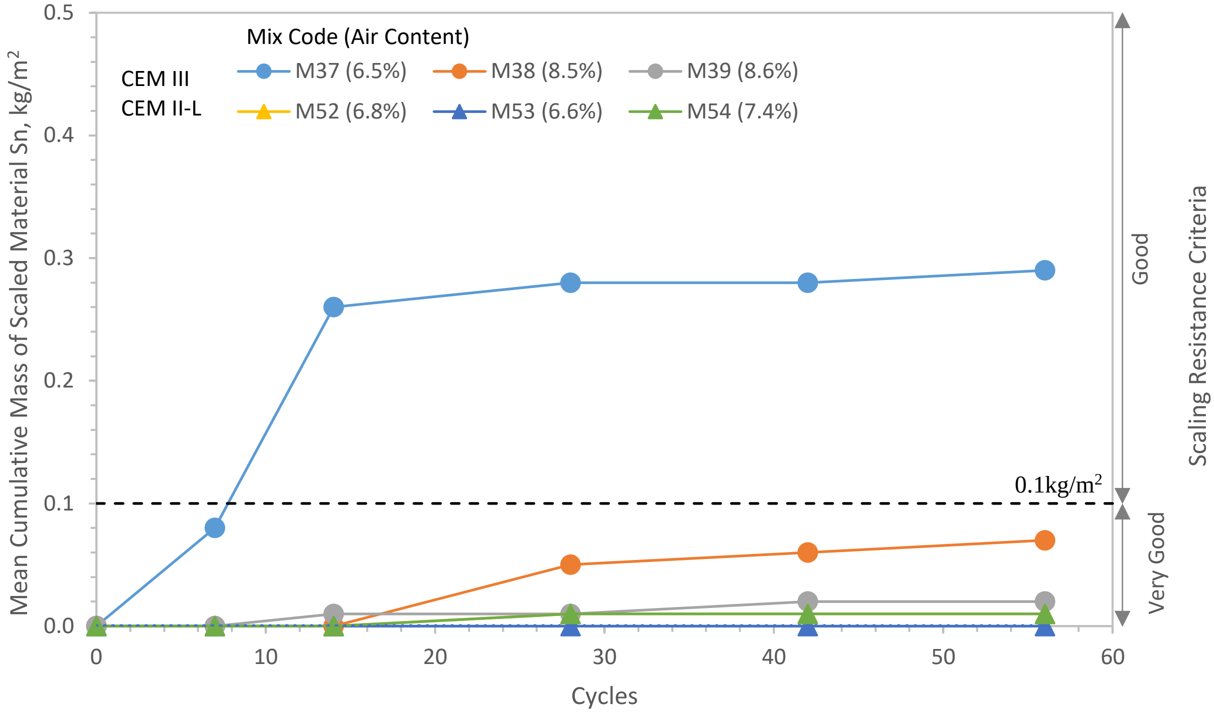


Figure 5.18 Freeze-thaw scaling of CEM III/A and CEM II/A-L series 3 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.7 Scaling criteria results for 40 MPa strength CEM III/A and CEM II/A-L series 3 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m^2/cycle	[1]Scaling Criteria
	Concrete Type	w/c	Air Content, %					
M37	CEM III/A	0.44	6.5	0.29	na	1.04	0.0900ln(x)	Good
M38	CEM III/A	0.44	8.5	0.07	na	1.40	0.0379ln(x)	Very Good
M39	CEM III/A	0.44	8.6	0.02	na	2.00	0.0094ln(x)	Very Good
M52	CEM II/A-L	0.45	6.8	0.06	na	1.20	0.0059ln(x)	Very Good
M53	CEM II/A-L	0.45	6.6	0.05	na	1.00	0	Very Good
M54	CEM II/A-L	0.45	7.4	0.05	na	1.67	0.0059ln(x)	Very Good

na – not applicable
[1]In accordance with SS 137244

At 60 MPa, the samples have a mass loss of 0.24kg/m^2 for CEM I non air entrained whilst the largest mass loss from the varied air content (Figure 5.17) was 0.04kg/m^2 which is from CEM II/B-V concrete with an air content of 6.8%. This illustrates that even with the increased strength does not necessarily mean that the samples would have the capability to withstand freeze-thaw attack whilst air entrainment provides very good scaling resistance.

There were outliers regarding the CEM III/A concretes. CEM III/A have shown to provide very good freeze-thaw resistance for both air and non-air entrained samples and has shown to out-perform CEM I. When the air contents of the concretes are increased beyond the maximum defined in the standards, CEM III/A begins to *under-perform* compared to the others, especially CEM II/B-V. This can be justified by CEM III/A's inability to work with the air entrainer and subsequently reduce the overall strength of the concrete. CEM III/A does not recognise air entrainer in the mix and although it is there and is being registered on the air void analyser, the admixture is not really needed. However, it was observed that during the study of the increased air content the strength of the concrete was minimally affected by the additional air content as shown in Figure 5.19.

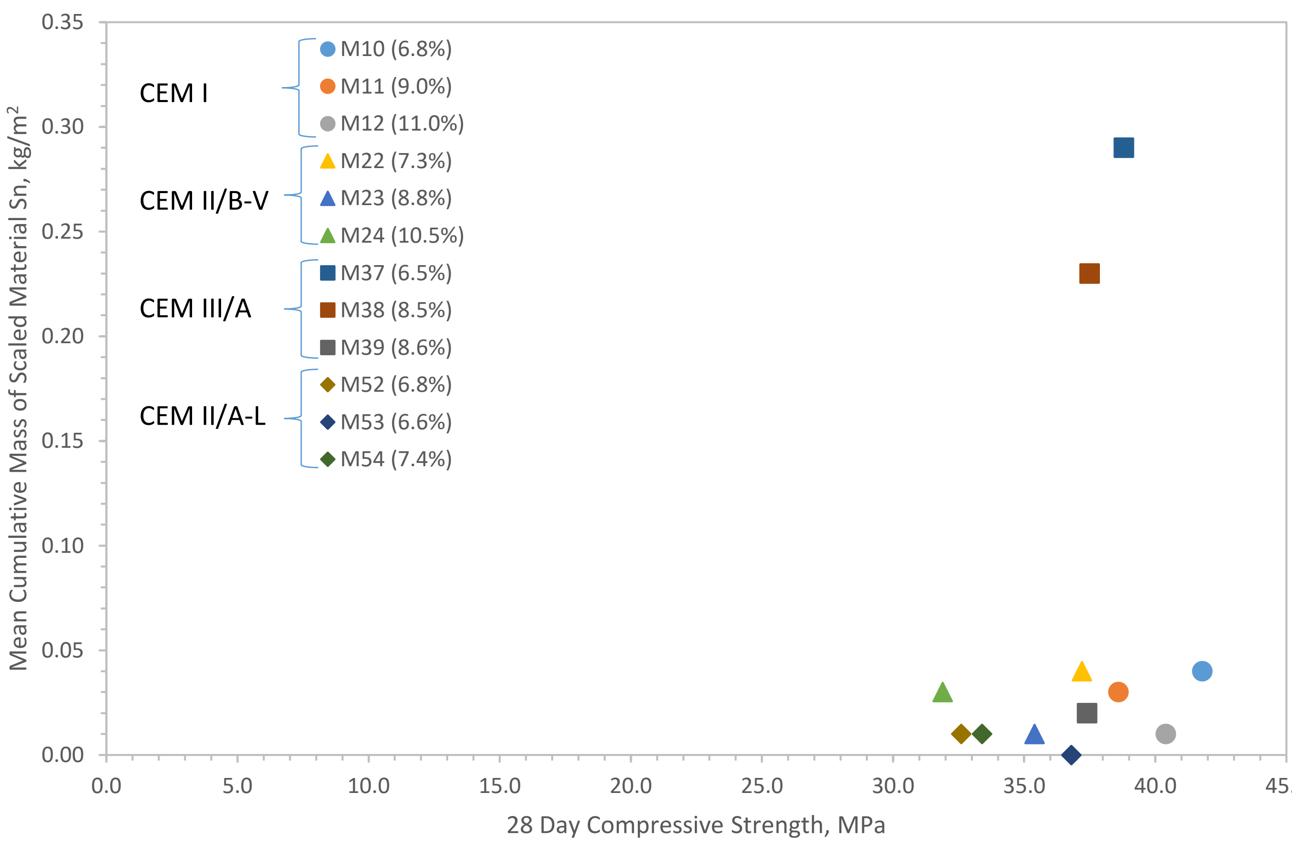


Figure 5.19 Comparison between freeze-thaw scaling and compressive strength of concretes with increased air content

CEM III/A is barely affected by the increased air content as the results show only a very minor decrease in the strength. The rest of the concretes follow the trend whereby when the air content is increased the strength decreases. However, when tested for freeze-thaw, the concretes surpass the requirements for freeze-thaw durability meaning that despite the reduction in the strength, majority of the concretes achieve a very good rating in accordance with SS 137244.

Also noticed from the results, particularly for CEM III/A and CEM II/A-L, is the plateauing of the air contents once it reaches a certain percentage. Whilst CEM I and CEM II/B-V both continue to increase in air content CEM III/A and CEM II/A-L have reached a point whereby continually adding more air entraining admixture would cause the workability to increase because of the side benefits of a superplasticiser and the air content remains the same but the strength still decreases.

5.4.2 The Effects of Air Void Parameters on the Scaling of Concretes with Different Air Contents

Series 3 looks at the influence of increased air content of different concrete types and how the increased air content affects the strength and freeze-thaw resistance. In the previous section it was established that increasing the air content does affect the strength significantly when higher contents are achieved. Although with the decrease in the strength the freeze-thaw performance was unaffected by the reduction in the strength loss.

This section looks at how the air void parameters from the increased air content influence the concrete's freeze-thaw performance. In the previous sections where Series 1 and 2 were studied (non-air and air entrained concretes respectively) it had been observed that when each of the air void parameters were compared to the freeze-thaw scaling results, there was very little correlation between them. Moreover, the one parameter which had been used for decades (spacing factor) to identify a concrete's suitability for freeze-thaw conditions turned out to produce results that in fact did not make sense, especially if they were compared to results from previous studies. Powers (1945) initially stated that if a concrete with a spacing factor less than 250μm then it would be able to withstand freeze-thaw. However, this was based on CEM I concretes only and since his work newly developed admixtures have changed the dynamic within a concrete's microstructure (as previously discussed).

Increasing a concrete's air content does influence how the concrete is going to behave and change the air void parameters within. Figure 5.20 shows the scaling results for various concrete types with different air contents against the different parameters which are calculated from the air void analyser. As the results show the concretes closely packed near the bottom meaning that there is minimal scaling, although there are two outliers from the CEM III/A group which is not unexpected because CEM III/A is known to have a high performance in regards to freeze-thaw, even without air entrainment, which is one of the reasons why it is used in freeze-thaw conditions. Even though the results for the spacing factor have been dismissed due to their unreliability, there is still premise to review the results to gauge how the results will correspond with the other parameters, and as shown form Figure 5.20b, the spacing factor is very low indicative with the increased air contents. With the higher air contents this means that the void frequencies are also much higher which is consistent with there being more voids.

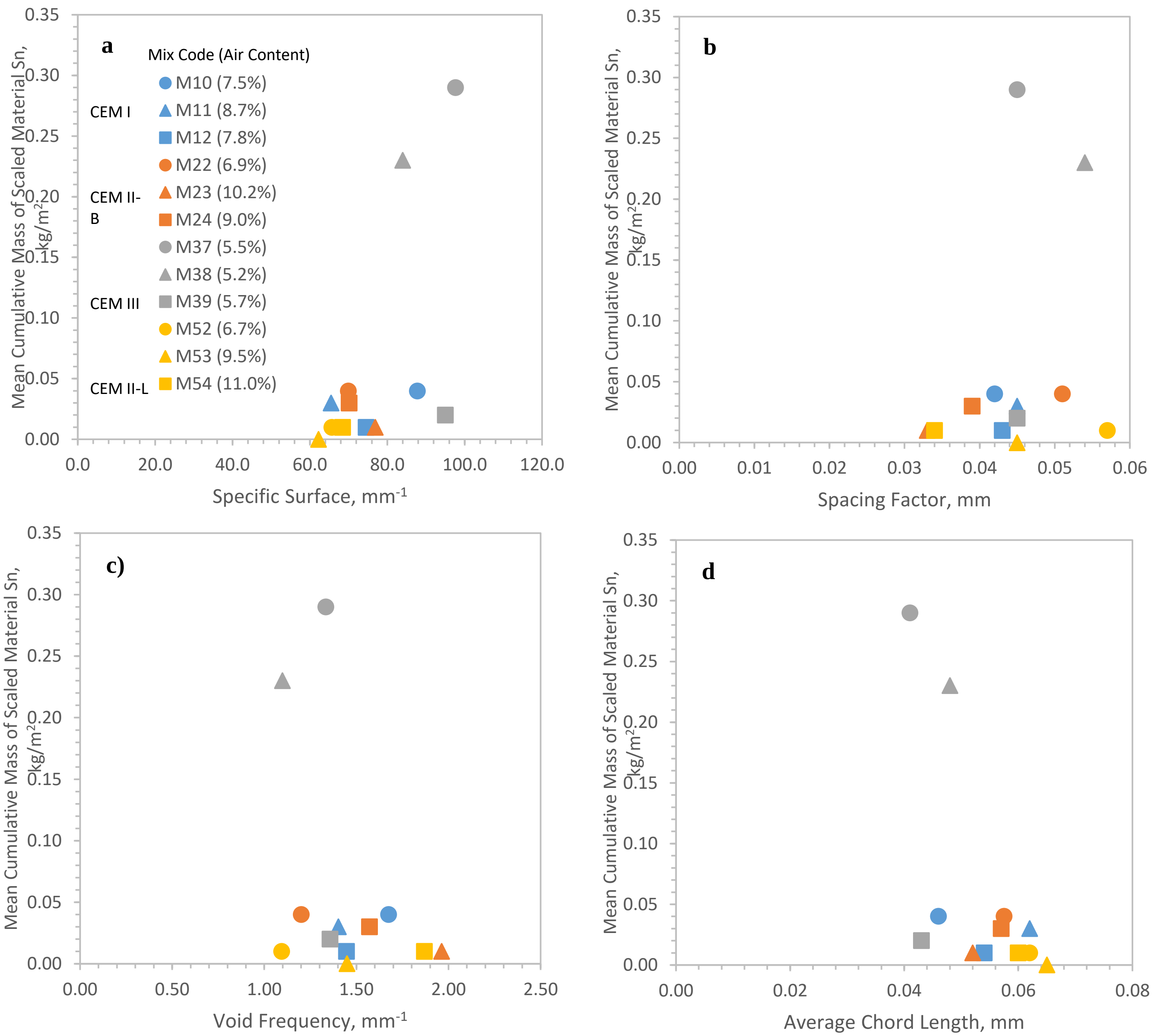


Figure 5.20 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of concretes with different cement types and air contents (Series 3)

5.5 Freeze-Thaw Scaling of Concretes with Varied Cement Addition Contents (Series 4)

Series 4 concretes consisted of only concretes containing replacement material as this would be varied to determine the impact this has on the freeze-thaw durability. Each of the concretes had replacement contents set at the maximum for freeze-thaw as stated in BS 8500. However, considering more sustainable options are needed in replacement of CEM I then increasing the current maximum additions would subsequently reduce CO_2 emissions.

Figure 5.21 and Figure 5.21 Freeze-thaw scaling of CEM II/B-V, CEM III/A and CEM II/A-L Series 4 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.8 show the results for the freeze-thaw testing along with the values at 56 cycles and the rate of deterioration for each of the samples based on the data collected. Based on the results shown, it can be said that all the concretes provide an acceptable scale rating (apart from one concrete) showing that the increase in the replacement content there is better performance for freeze-thaw. Although the results show a better durability, they are different than what was expected. The materials (particularly fly ash) have shown to deteriorate quicker in freeze-thaw due to the value of the loss of ignition (L.O.I) value. Though in this instance, the fly ash used for test had an L.O.I value of 5.1% which is close to the value of CEM I (4.6%) showing that it is not the L.O.I value. Although, in this section the total fly ash content used for testing has increased which may influence the amount of admixture available to the concrete.

The standardised replacement content values described in BS 8500 have shown to be durable during freeze-thaw attack provided the concretes are air entrained. This meant despite the standards detailing a maximum content for each material which have been designed for freeze-thaw, further increase in the maximum replacement has shown to be able to withstand scaling. Out of the nine concretes only one did not meet the acceptable scaling criteria. GGBS has increased freeze-thaw durability compared to fly ash and limestone whereby all the concretes are shown to provide a very good scaling rating which is tied to the basis that GGBS performs well when subjected any chloride ingress.

Comparing these results to their standardised counterparts shown in Figure 5.22, there are differences in the overall performance of these concretes, though there are not major differences when looking at the samples from a scaling perspective. However, when compared to their standardised counterparts then there were differences in the results. This means that a higher replacement content could be over the limit stated in BS 8500. However, one consequence of increasing the amount of replacement material is the reduction in the compressive strength due to lowering the CEM I content. For a given strength a cement content is calculated from a selected water content which defines the strength.

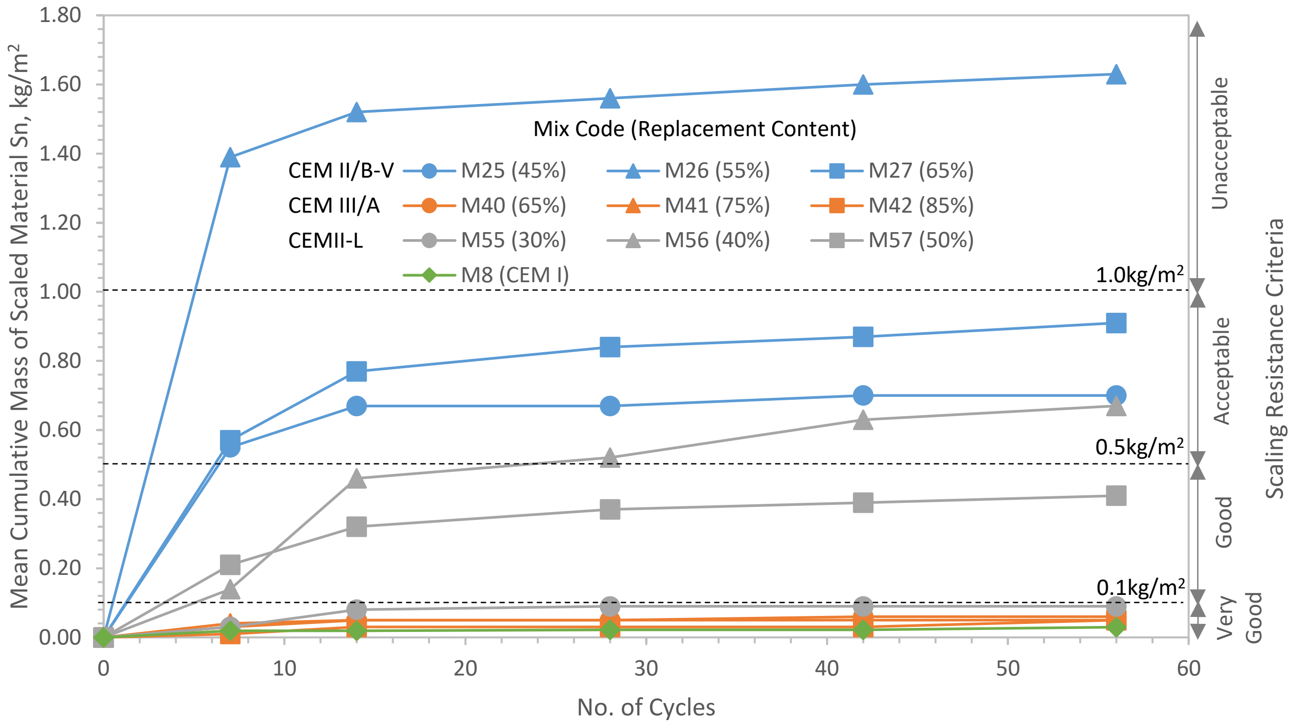


Figure 5.21 Freeze-thaw scaling of CEM II/B-V, CEM III/A and CEM II/A-L Series 4 concretes with the scaling resistance criterion detailed in SS 137244

Table 5.8 Scaling criteria results for CEM II/B-V, CEM III/A and CEM II/A-L Series 4 concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m²	Approx. Cycle No. of Limit Sn≥1.0kg/m²	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m²/cycle	[1]Scaling Criteria
	Replacement Content, %	w/c	Air Content, %					
CEM II/B-V								
M25	45	0.42	4.7	0.7	na	1.04	0.0657ln(x)	Acceptable
M26	55	0.41	4.5	1.63	0 – 7	1.04	0.1081ln(x)	Unacceptable
M27	65	0.39	4.5	0.91	na	1.08	0.1529ln(x)	Acceptable
CEM III/A								
M40	65	0.44	4.4	0.06	na	1.20	0.0136ln(x)	Very Good
M41	75	0.44	4.4	0.05	na	1.00	0.0042ln(x)	Very Good
M42	85	0.44	4.2	0.05	na	1.67	0.0146ln(x)	Very Good
CEM II/A-L								
M55	30	0.49	4.5	0.09	na	1.00	0.0268ln(x)	Very Good
M56	40	0.49	4.4	0.67	na	1.29	0.2388ln(x)	Acceptable
M57	50	0.49	4.3	0.41	na	1.11	0.0921ln(x)	Good

na – not applicable
[1]In accordance with SS 137244

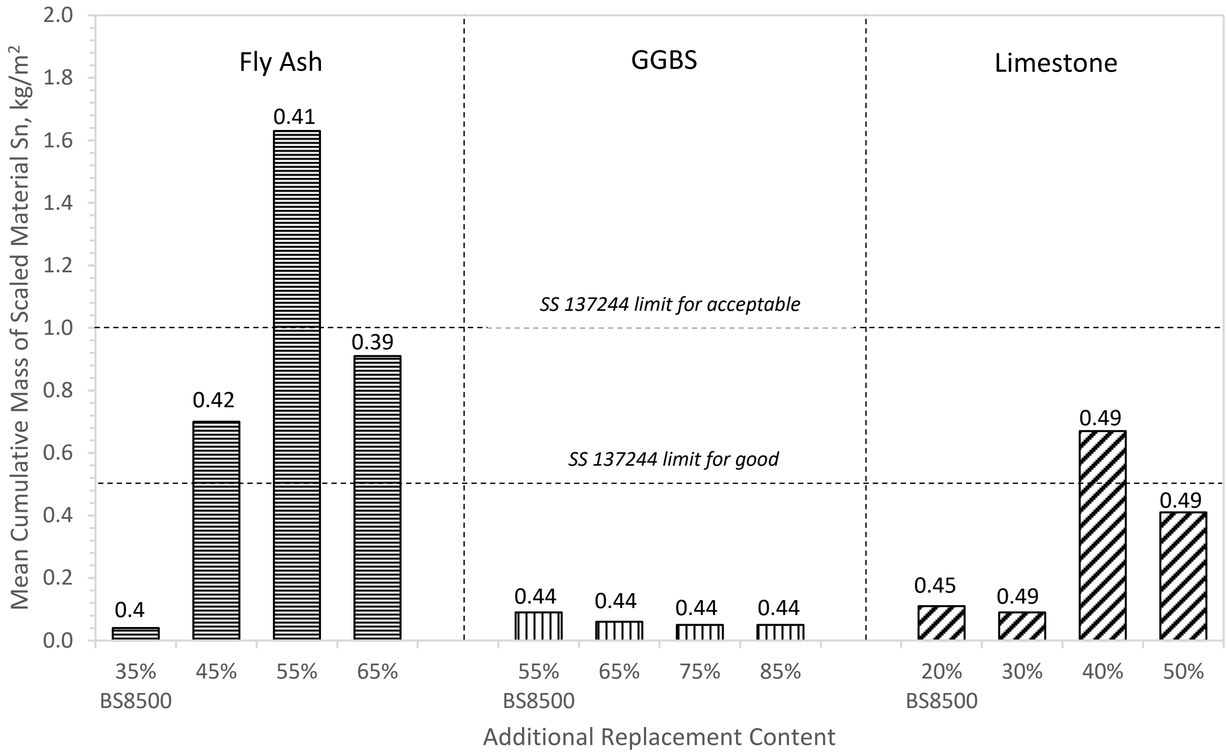


Figure 5.22 Comparison between the freeze-thaw results of different concrete types with various cement addition contents at 40 MPa strength measured against their respective maximum allowance in accordance with BS 8500 and the water/cement ratio above each bar

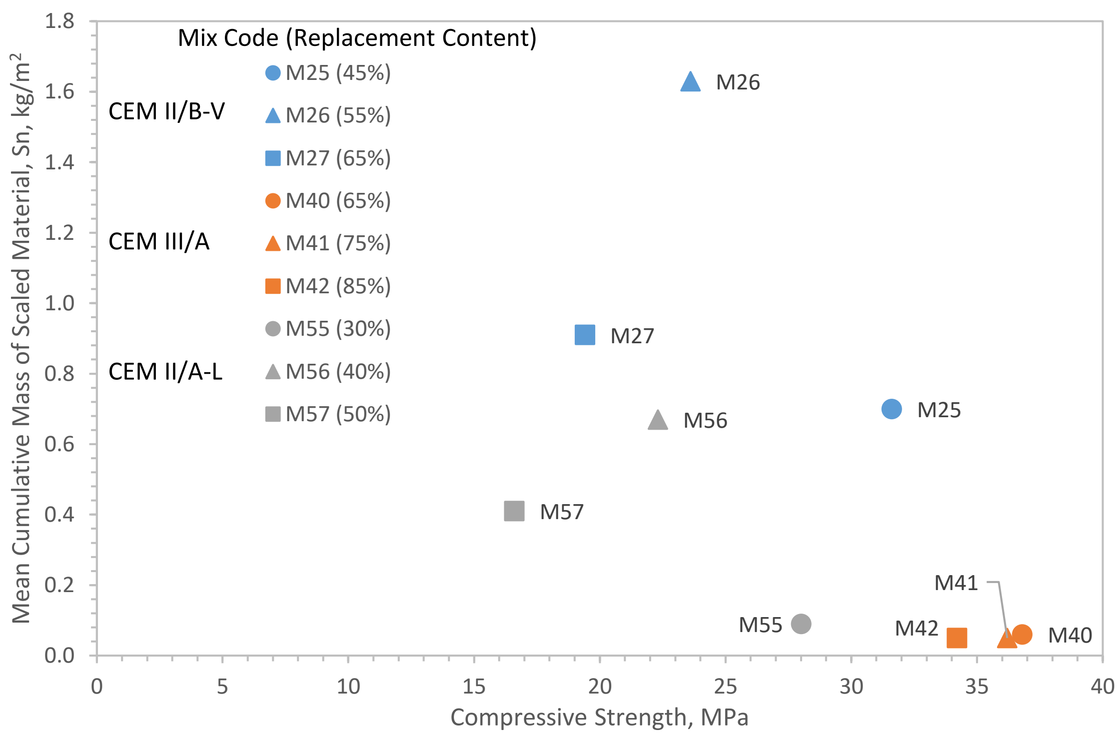


Figure 5.23 Comparison between freeze-thaw scaling and compressive strength of concretes with increased maximum replacement content

There are many properties which justify the strength of the concrete, mainly the water/cement ratio which dictates the strength. However, as Figure 5.22 shows the water/cement ratio remained constant for the mixes so the strength and the scaling loss should be the same regardless of cement addition content but the results show different contradicting the earlier statement as the cement addition content does in fact affect the scaling loss due to the amount of CEM I.

Most concretes rely on CEM I and admixtures to achieve a high strength at 28 days and reducing the CEM I content potentially increase the time taken for the concrete to reach initial strength. As shown in Table 3.6, Table 3.7, Table 3.8 and Table 3.9, the strengths of the materials decreases with the increase in the replacement material after the specified limit dictated in BS 8500. However, as shown in Figure 5.23, even with the decrease in the compressive strength, the concretes still had the capacity to withstand freeze-thaw scaling and achieve a very good scaling rating.

5.5.1 The Effects of Different Addition Materials on the Air Void Parameters and Scaling of Concretes

Increasing the additional content whilst reducing the CEM I content has been shown to have significant effects on the concretes strength and freeze-thaw durability and whilst the strength of the concrete did suffer as a result. Though, from the results shown in Figure 5.24a to d there seem to be an inverse correlation in the results when compared to their respective parameters. Whilst the increase in the replacement seen the freeze-thaw performance decrease, the air void parameters of the concrete appear to improve. For example, the results for CEM II/B-V freeze-thaw resistance decreased with each incremental increase, whilst the air void parameters such as the specific surface and spacing factor provided results which indicate that the concretes would in fact be able to withstand freeze-thaw attack with further replacement.

Arguably this would relate to the percentage content of fly ash in the concrete and its tendency to absorb the air entrainer. Previous studies (Ahmed, et al., 2014; Ahmed & Hand, 2014) have shown that with the addition of fly ash in concrete the requirement for air entrainer increases exponentially due to its high absorption rate. With the high absorption rate, it is still possible to maintain the same level of entrainment as with CEM I concretes be it more expensive regarding admixture volume. Again, this relates back to the increased microstructural properties, thus, the air void characteristics of the concrete and how they increase when a higher replacement content is used.

Furthermore, the particle sizes of the replacement materials influence both the microstructural properties and the freeze-thaw resistance. Comparing the particle sizes between CEM II/B-V and CEM II/A-L, there is a direct link between the size of the particles for the material and the freeze-thaw resistance.

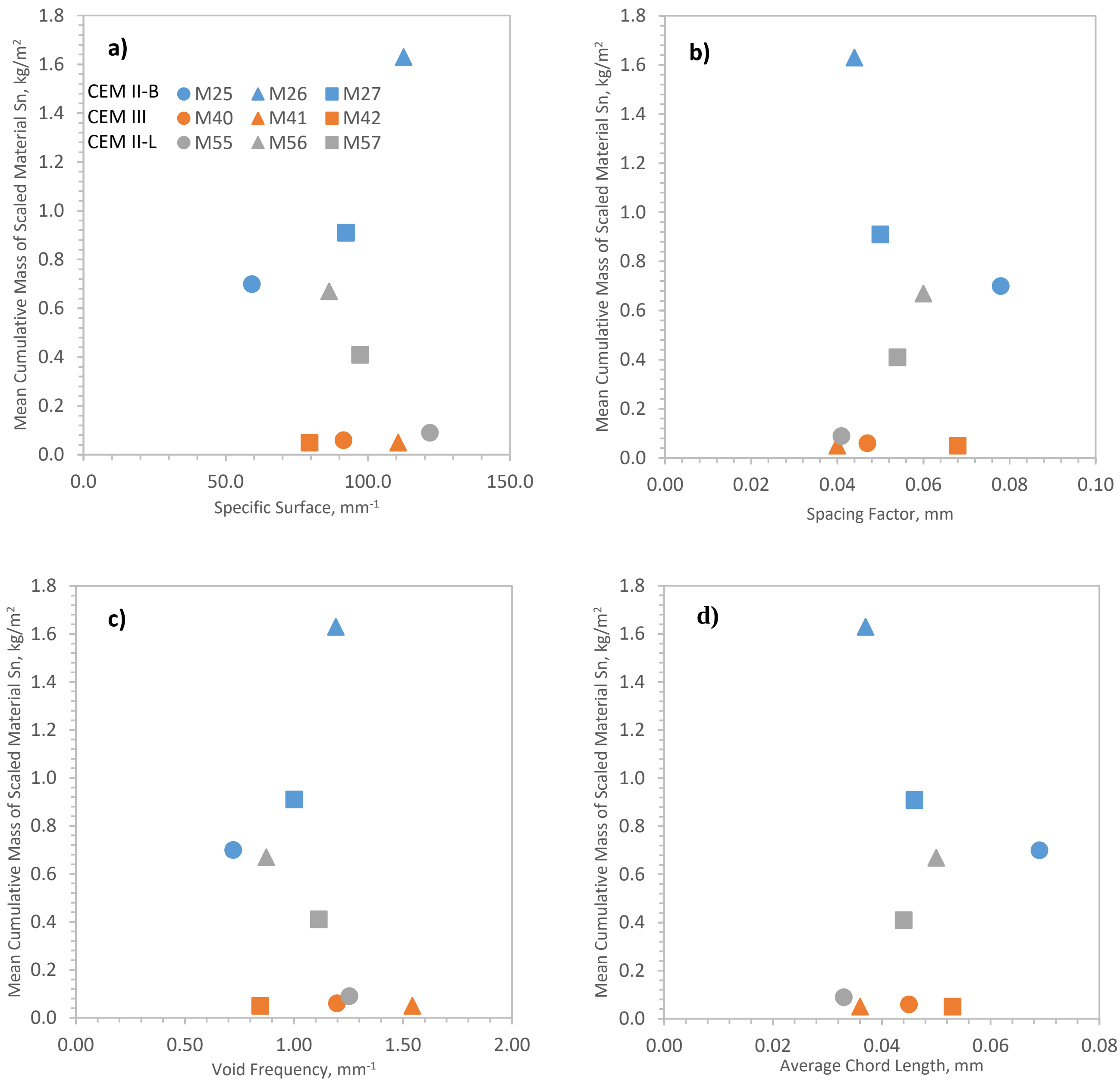


Figure 5.24 Influence of the air parameters a) specific surface; b) spacing factor; c) void frequency and; d) average chord length measured in hardened concrete on the freeze-thaw scaling of concretes with different cement types and air contents and replacement content percentages (Series 4)

Reviewing the strength-scaling plot (Figure 5.23) it is observed that both materials share similar trends regarding the strength loss with CEM II/B-V scaling loss being more than double CEM II/A-L. Even if a comparison is done between a higher CEM II/A-L replacement (for example 50%) and a lower CEM II/B-V replacement (for example 35%), CEM II/A-L still outperforms CEM II/B-V. This then relates to the particle size of the replacement material.

The analysed fly ash have shown that there are larger particles for four out of the five fly ashes ranging between 16µm and 25µm compared to other cementitious material including CEM I, GGBS and limestone (15.9µm, 11.0µm and 5.9µm respectively) which would explain the difference however from the particle size distribution results it is not only this as the distribution for the fly ash used has an overall size distribution less than limestone.

The freeze-thaw performance of CEM III/A is seen to not be affected by the increase in replacement material. In fact, despite the increase in the replacement content, the scaling for each of the different contents are very similar. This is also because the strengths of these concretes were almost equal. However, the microstructural properties of the concretes are different as shown in Figure 5.24.

All the concretes were dosed with the same amount of admixture but from the figure it is clear there is a difference in the air void parameters from the increased cement addition content. M40 – M42 (GGBS) did not show any variation regarding the scaling loss the spread of the data over the four graphs shows an interesting depiction. All four graphs compare an air void characteristic (specific surface, spacing factor, void frequency and average chord size) against the mean scaled loss of material and from the graphs there is a similar trend in the distribution of the results. Since the scaling loss is the same then the data on the y-axis will not change but it would be expected that the data on the x-axis would change with the different parameters. Whilst that may be true for most in this case it would be difficult because each of the parameters are calculated from the previous as detailed in BS EN 480-11 making it difficult to compare the parameters to each other to determine the better choice. This is seen for the CEM II/B-V and CEM II/A-L concretes.

5.6 Determining the Usefulness for the Microair Content Parameter

According to BS EN 480-11 the micro air content refers to the voids sizes which are less than 300µm, then anything above does contribute to the protection however once above 500µm the void size tends towards the entrapped air range due to coalescence and any air may not have been removed via vibration. A high microair content would mean a high durability rating for freeze-thaw. Figure 5.25 shows how the microair content influences the overall for each cement type.

As shown, the microair content ranges from 3 to 4% air content whilst the remaining air content is attributed to the larger entrained air voids and entrapped voids. The microair contents for each of the concretes varies slightly differently with CEM II/B-V having the lowest microair content. This relates to the fly ashes absorption of the air entraining admixture due to the carbon content and the particle sizes allowing for microair voids to form between the particles.

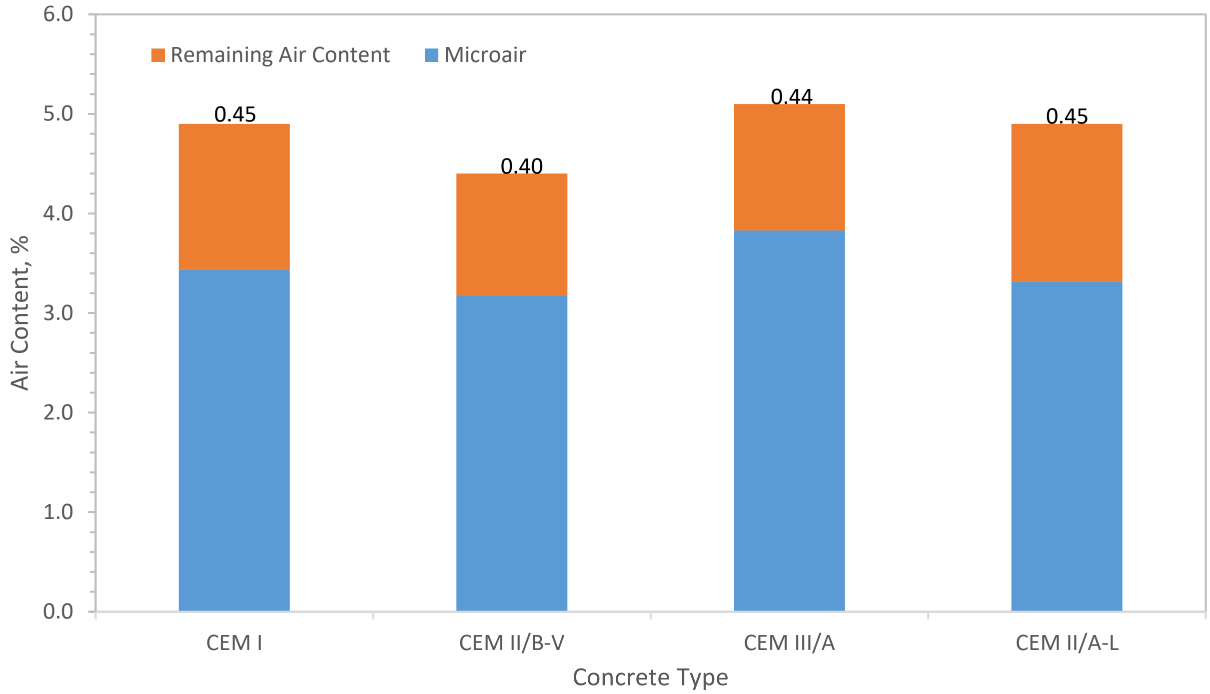


Figure 5.25 The microair contents for different concretes with the same 40 MPa strength plotted against the average diameter particle size for each cement type and the water/cement ratio displayed above each bar

On the other hand, the particle size distribution for fly ash varies depending on the fly ash used compared to CEM I, GGBS and limestone. Overall, the PSD of CEM I, GGBS and limestone show a lower D_{90} of 44.5µm, 32.7µm and 19.6µm respectively, allowing less void space to be available for water infiltration. whereas the fly ash had a larger particle size of 67.5µm giving more void space for the microbubbles to fill the voids. Though it is possible that smaller particles (fly ash, CEM I and fine aggregate) could potentially fill these voids, due to the large distribution of particle sizes it would be difficult to ensure all these voids are filled before subjection to freeze-thaw.

Although microair provides the majority of the air content in the concrete due to the size of the voids, there is a downside to using the microair values, mainly relating to how the micro voids affect other air void parameters, especially spacing factor. The microair content is the air content of the measured voids that are 300µm or less. The problem with using this parameter is that when the voids are counted from a sample, the smallest void sizes (ranging from 10-30µm) make up a high number of the total voids. Figure 5.26 shows how the number of voids for each of the different void ranges.

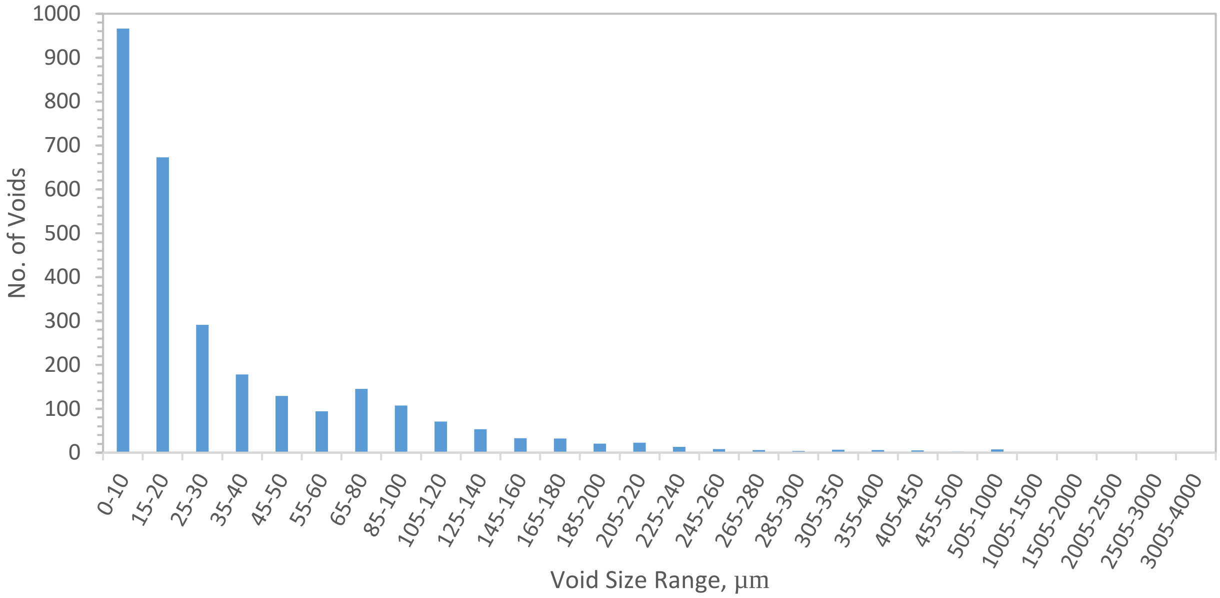


Figure 5.26 Number of voids in each void size range for an air entrained 40 MPa CEM I concrete

As shown in the figure, there are many voids within the 10-30µm range that add up to approximately 67% of the total void count. Because of this the spacing factor is significantly influenced by the number of voids within the concrete sample. As previously stated, the spacing factor is calculated by measuring the distance between the voids and the average is taken. So, with majority of the voids being accounted for within a small size range it means that the spacing factor will reduce in response to this due to there being a lot of voids that are in the small size range. The reduction in the spacing factor then does not show the true value of the concrete, especially concretes which do not have air entrainer.

Using the microair content does provide a general idea on the air content of the concrete but it could be manipulated to provide a better value of the air content. Considering only the air content of the void size range 10-30µm, even though most of the voids counted are in this range size they only account for 0.69% of the total air content. According to the standard the microair content is only accountable until 300µm but there is no definitive definition for the maximum void size before the bubbles change from being air entrained to entrapped air. Looking at the microair results in Figure 5.26, increasing the maximum microair void size from 300µm to 500µm and remove the results from the size range 10-30µm then the air contents would change from 4.1% to 3.8% and although the total air contents only vary slightly, the total number of voids for the microair changes significantly from 67% to 33% of the total voids counted. This shows that majority of the voids are in fact in the 10-30µm and influences the spacing factor.

5.7 Freeze-Thaw Scaling of Concrete Containing Non-XF4 Coarse Aggregate

One of the study areas looked at during the research project is the effects of various aggregate types on the performance of concrete during freeze-thaw. Majority of the work has been focused on concrete containing granite as the coarse aggregate with a classification of MS_{18} (magnesium sulphate rating of 18). Lightweight aggregate has also been studied and is covered in Chapter 6.

Using gravel in concrete is not uncommon, however, using this type of aggregate may increase the likelihood that the concrete can deteriorate during freeze-thaw due to the porosity of the aggregate allowing water to infiltrate the voids and freezing causing deterioration of the aggregate. Natural local gravel was tested using the magnesium sulphate test and even though the material is not suitable for XF4 conditions, it was still applicable to XF3 conditions (not passing the MS_{25} limit – 25% mass loss). Using the four cement types (CEM I, fly ash, GGBS and limestone) as above, a series of concrete both air and non-air entrained were test for freeze-thaw durability. Figure 5.27 shows the cumulative mass loss for each of the concretes.

As the figure illustrates, there is more mass loss with non-air entrained concretes which is consistent with the results shown for the concretes containing granite. Moreover, CEM II/B-V concretes show to have more mass loss with freeze-thaw compared to the rest for both air and non-air entrained samples. This is because CEM II/B-V have been established to perform poorly during freeze-thaw testing and using a weaker coarse aggregate only increases the mass loss.

Table 5.9 details the mix characteristics along with the numerical freeze-thaw results and the scaling criterion. In accordance with SS 13 72 44, the scaling criterion dictates the resistance a concrete has to the freeze-thaw test. As Table 5.9 shows, the air entrained samples all remain below the *Acceptable* limit. GV7 has a higher mass loss compared to the rest as this mix has GGBS as the addition and it has been established that GGBS concretes containing air entrainer does not provide the protection for freeze-thaw as it would for CEM I.

As for the non-air entrained mixes, GV1 and GV2 are classed as unacceptable as they pass the 1.0kg/m^2 benchmark. GV3 and GV4 are both in the *Acceptable* band meaning that using GGBS and limestone replacements in concrete without air and locally sourced gravel for the coarse aggregate provides sufficient protection to prevent an unacceptable deterioration.

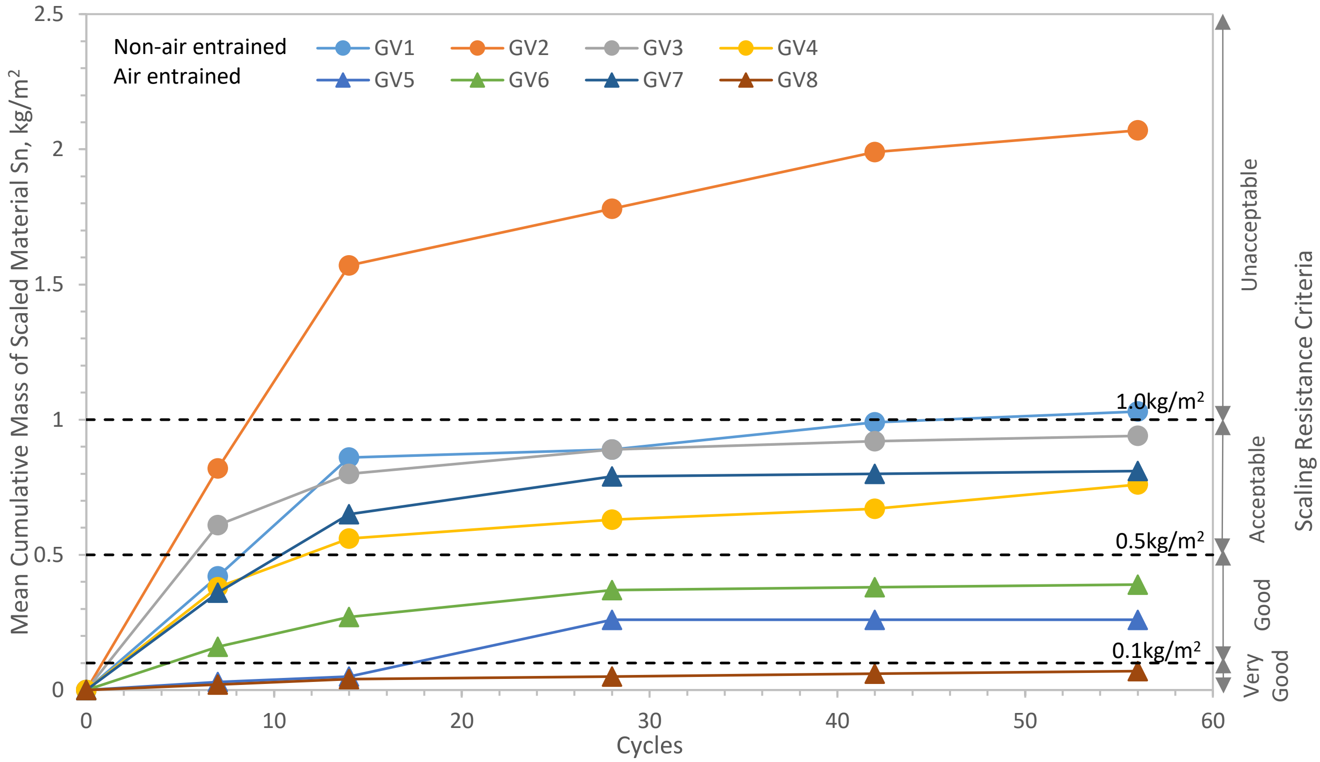


Figure 5.27 Freeze-thaw scaling of various concretes containing gravel as coarse aggregate with the scaling resistance criterion detailed in SS 137244

Table 5.9 Scaling criteria results for 40 MPa strength concretes with various cement types containing gravel as coarse aggregate along with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m²	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m²	Sn_{56}/ Sn_{28}	Rate of Deterioration, kg/m²/cycle	Scaling Criteria
	Concrete Type	**w/c**	**Air Content, %**					
Non-Air Entrained								
GV1	CEM I	0.54	1.3	1.03	42 – 56	1.16	0.2659ln(x)	Unacceptable
GV2	CEM II/B-V	0.47	1.4	2.07	7 – 14	1.16	0.5714ln(x)	Unacceptable
GV3	CEM III/A	0.52	1.5	0.94	na	1.06	0.1543ln(x)	Acceptable
GV4	CEM II/A-L	0.54	1.5	0.76	na	1.21	0.1653ln(x)	Acceptable
Air Entrained								
GV5	CEM I	0.45	4.5	0.26	na	1.0	0.1324ln(x)	Good
GV6	CEM II/B-V	0.4	4.4	0.39	na	1.05	0.1133ln(x)	Good
GV7	CEM III/A	0.44	4.5	0.81	na	1.03	0.212ln(x)	Acceptable
GV8	CEM II/A-L	0.45	4.7	0.07	na	1.40	0.0226ln(x)	Very Good

na – not applicable

The differences between these results can be attributed to the high porosity of the aggregate meaning that due to the high volume of pores in the aggregates, there is a higher possibility that it is the aggregate that is deteriorating rather than the cement paste. The underlying issue with using gravel is its petrography where it is not just simply one material like granite or limestone but rather a mixture of different materials which are amalgamated as one class of material deemed natural local gravel. Among those materials is red sandstone particles that are known to be weak before mixing into concrete and since it is also very porous it was this type of material which probably deteriorated first.

The argument can be made that because the gravel material is porous it would allow more water to fill the voids within the aggregate first instead of the cement paste. Moreover, because of the size of the voids these tend to freeze first before the smaller voids leading to the scaled material being from the gravel.

Comparing XF4 and non-XF4 Compliant Aggregate Freeze-Thaw Data

When the results from the granite and gravel are plotted against one another, there are some interesting points that must be addressed. Figure 5.28 shows the data for compressive strength plotted against cumulative mass loss for the granite and gravel counterpart, non-air entrained mixes. As the figure depicts, the overall results show that the mass loss for granite is less than gravel. CEM I (M3 and GV1) are relatively similar in mass loss even though M3 has a 14% increase in strength. This can result in 'pop-outs' of aggregates during the test.

CEM II/B-V (M15 and GV2) mixes have the greater mass loss than all the others containing the same type of aggregate, especially GV2. As it is already noted that fly ash concretes have a higher rate of deterioration, the addition of gravel increases the mass loss by 40% compared to granite which confirms that using a porous aggregate like gravel increases the deterioration of the sample as the aggregate also succumbs to the ice expansion. Furthermore, during the first few cycles of the test it was observed that the aggregate deteriorated first before the cement paste. The meant using gravel as the coarse aggregate only added to the mass loss.

The mass loss between the aggregates for CEM III/A (M30 and GV3) was significant with a simple changing of the coarse aggregate. A strength difference of 15% is seen showing that the aggregate contributes 15% more to the compressive strength, whilst the mass loss shows a major difference between the aggregates of 90%. It can be said that for concrete containing GGBS, the increase in the mass loss can be attributed to the aggregate used.

CEM II/A-L (M45 and GV4) results show similarities between the compressive strength. Comparing the strength, there is a difference of 3% which is small and the mass loss difference of 55% between the materials which can be associated with the aggregate choice as seen with CEM III/A.

Figure 5.29 shows the comparison between the granite and gravel mixes containing air entrainment. Aforementioned, the concrete containing gravel as the coarse aggregate remain below the 1.0kg/m^2 limit, however, there is more mass loss compared to the granite. This coincides with the non-air entrained results whereby more scaling is observed due to the high porosity of the gravel. The following outlines the difference in the mass loss between granite and gravel:

- CEM I (M8 and GV5) mixes show that the gravel mix had 88% more mass loss from scaling;
- CEM II/B-V (M20 and GV6) sees a 90% difference in scaling;
- CEM III/A (M35 and GV7) has an 89% difference, and;
- CEM II/A-L (M50 and GV8) mixes show a difference of 36% with GV8 performing better than M50.

From the results described above, the gravel influences the freeze-thaw deterioration even with the addition of air entrainment and therefore careful selection of aggregates is needed for freeze-thaw resistance in accordance with BS 8500 and BS EN 1367-2 (Magnesium Sulphate test).

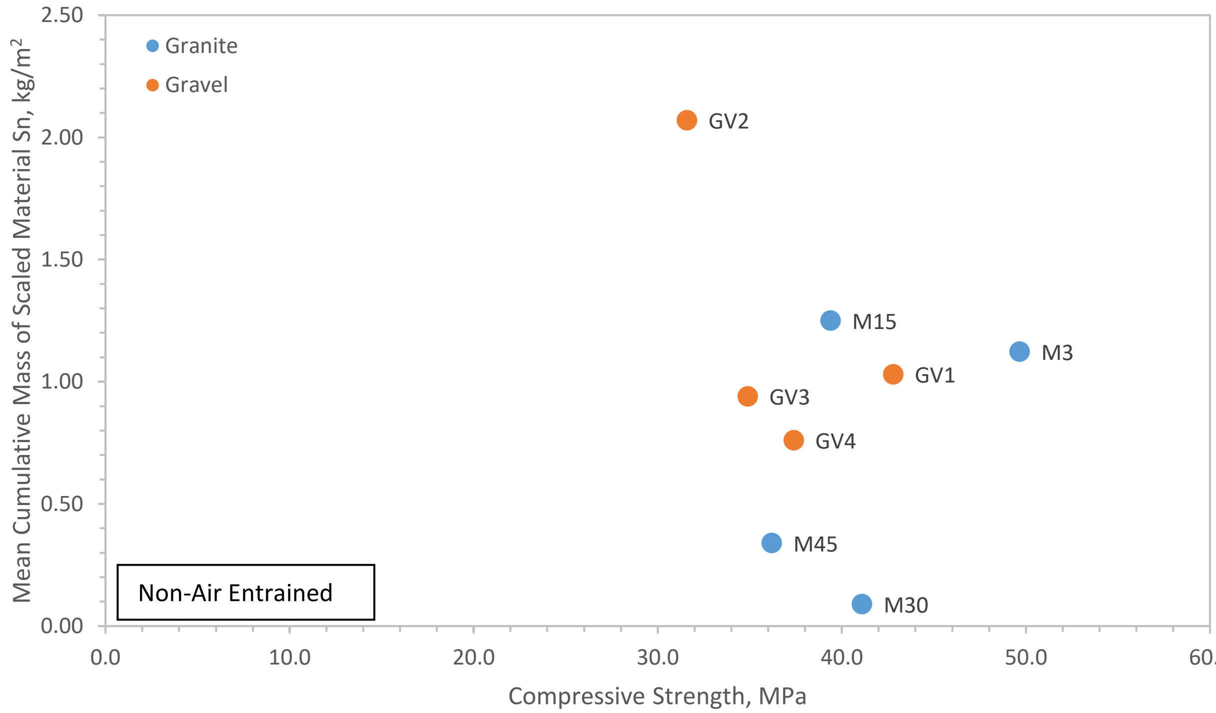


Figure 5.28 Compressive strength plotted against freeze-thaw scaling data for granite and gravel non air entrained mixes

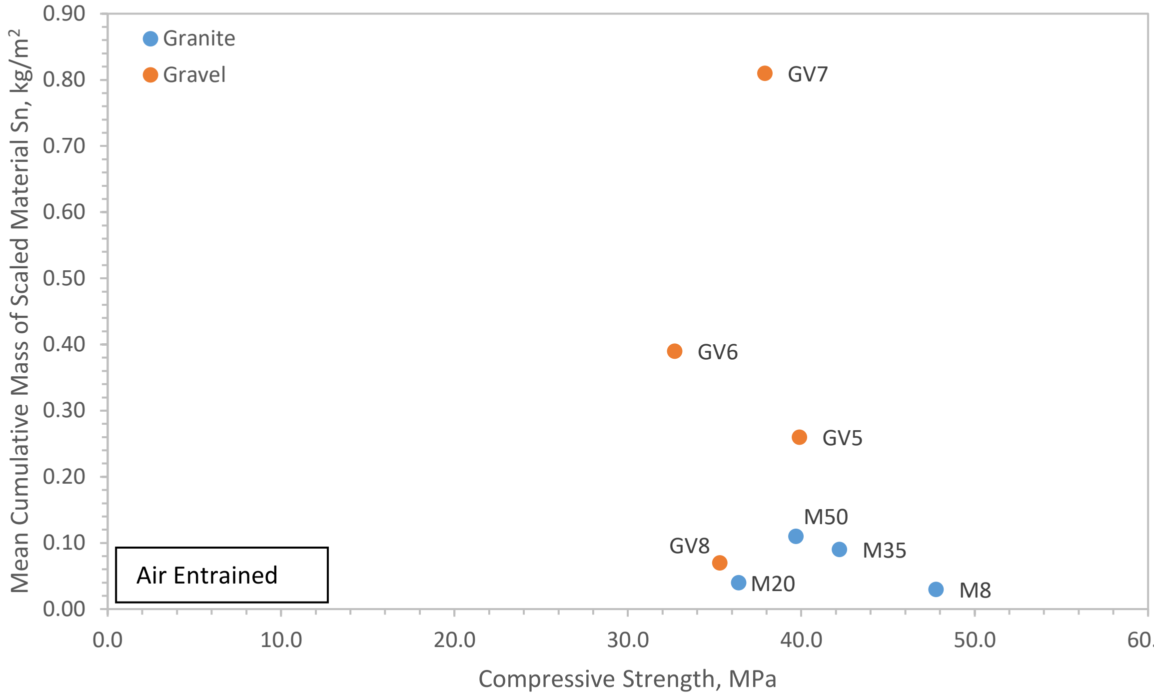


Figure 5.29 Compressive strength plotted against freeze-thaw scaling data for granite and gravel air entrained mixes

5.8 Freeze-Thaw Resistance of Typical UK Concretes Produced by Industry

A series of concretes were produced from industry contractors and were tested under the same conditions as laboratory concretes to compare whether similar scaling seen during laboratory testing were seen from the industry concretes. Figure 5.30 shows the scaling results for the industry concretes along with Table 5.10 which details the rate of deterioration and the scaling criteria in accordance with SS 137244.

As the figure illustrates, the concretes were tested for freeze-thaw resistance and, as seen during the laboratory testing, CEM I and CEM III/A concretes were able to withstand freeze-thaw conditions. CEM II/B-V also seen similar scaling loss compared to laboratory concretes. Furthermore, it is common that industry produced concretes meet their target strength plus a margin to ensure the characteristic strength is achieved and is capable to withstand freeze-thaw attack. Also, it is common that industry increase the air content for the same reason.

Comparing the laboratory results to the industry produced concretes is slightly more difficult because there are a number of parameters which can be used to analyse and compare for freeze-thaw such as the compressive strengths, cement type and replacement content percentage and air content for fresh and hardened concrete. Trying to identify the best comparison requires selecting different concretes which have similar results for each of the parameters. In doing so the concretes which are being used to compare to the industry will differ for each comparison.

The best option for comparing the concretes would be identify the concretes which closely match in strength and investigate what variations are observed. Figure 5.31 shows the comparison between the matching strengths for laboratory and industry produced concretes against their respective scaling results. From the figure there is a correlation between the strength and scaling results (as previously stated) and there is also a comparable comparison between the laboratory and industry concretes. The results show with similar strengths the scaling loss relatively close but there are differences also. M21 and IC-M05 show to have the same mass loss from scaling but the strengths are different by 7 MPa. This relates to the type of fly ash used for the concrete.

When it comes to concrete having the same mass loss from scaling, yet the strengths are different it can be identified that there is more air entrainer in one compared to the other which is understandable as more air entrainer means less strength. In the case of M21 and IC-M05 the results show that for the hardened air content there is difference a of 0.8% (4.6% and 3.8% respectively) meaning that the extra air content has caused a reduction in the strength by nearly a 1:0.1 ratio. M36 and IC-M03 both have scaling of 0.07kg/m^2 but have a strength difference 8 MPa. There is more air entrained in the industry concrete and a higher water/cement ratio compared to laboratory concrete, however, IC-M03 has a 50% addition value for GGBS whereas M36 has 55% replacement resulting in the difference in the results shown.

M7 and IC-M02, both being CEM I concrete, show little difference regarding the strength but there is a difference for the scaled material. Although M7 produces a good rating for freeze-thaw there is still a noticeable gap in the results which is due to the reduction in the strength. Even with a decrease in the strength by 2 MPa, provides enough of a difference that there is more scaled material for the laboratory concrete.

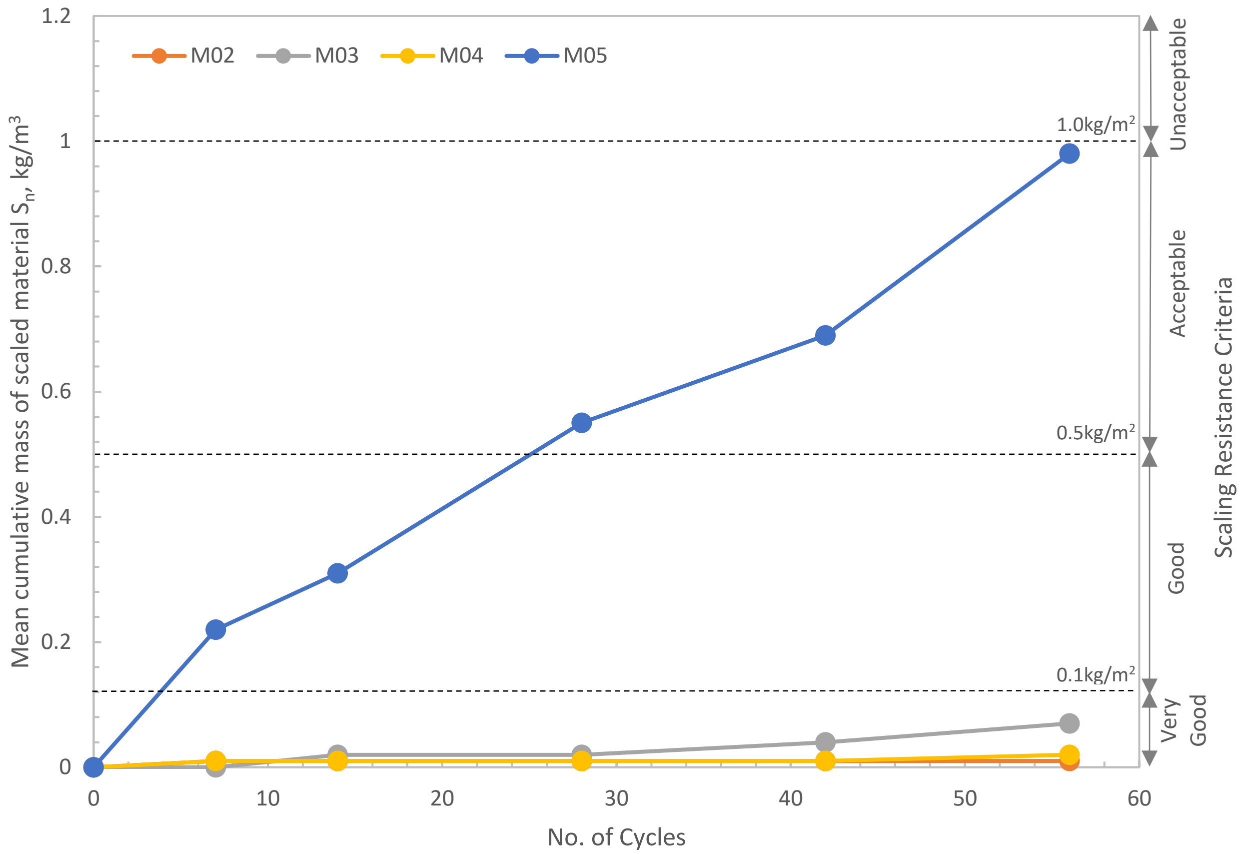


Figure 5.30 Freeze-thaw scaling of industry produced concretes with the scaling resistance criterion detailed in SS 137244

Table 5.10 Scaling criteria results for industry produced concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics		Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2	Sn_{56}/Sn_{28}	Rate of Deterioration, kg/m^2/cycle	Scaling Criteria
	Concrete Type	w/c					
IC-M02	CEM I	0.55	0.01	na	1.00	0.01	Very Good
IC-M03	CEM III/A	0.42	0.07	na	3.50	0.0281ln(x)	Very Good
IC-M04	CEM I	0.45	0.02	na	2.00	0.0031ln(x)	Very Good
IC-M05	CEM II/B-V	0.38	0.98	na	1.78	0.3428ln(x)	Acceptable

na – not applicable

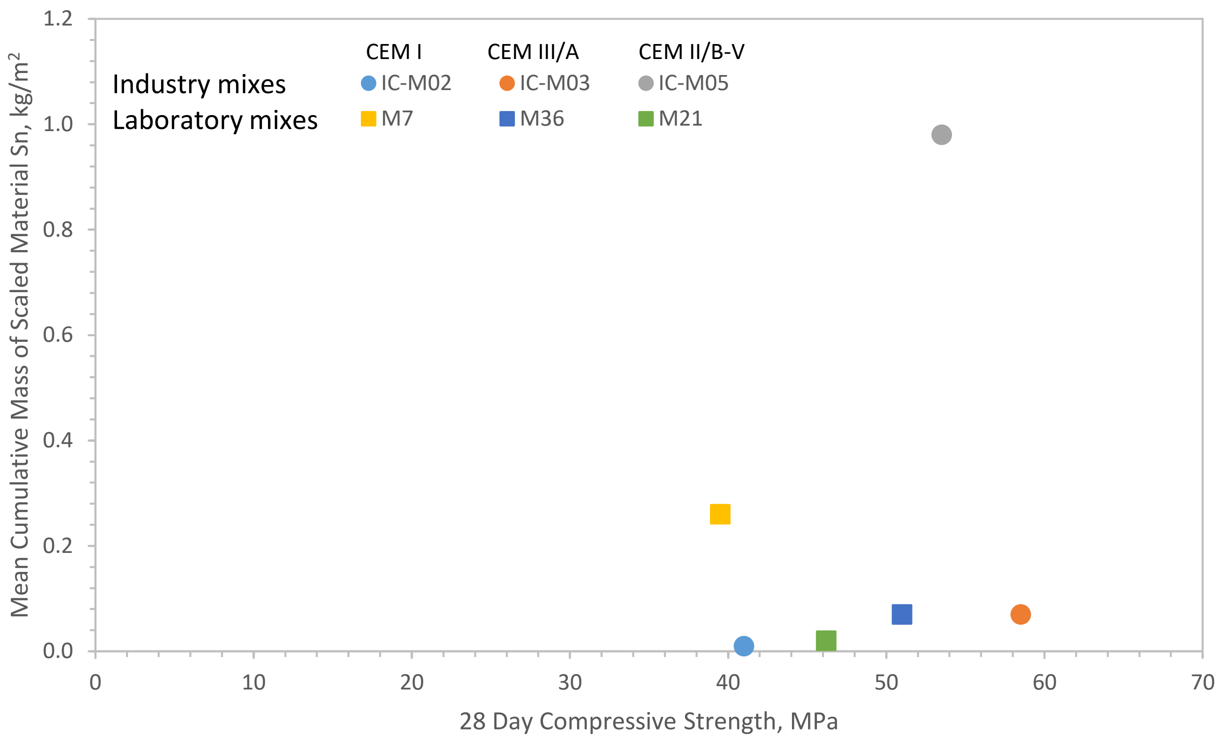


Figure 5.31 Comparison between the compressive strength and the scaling of the concrete for both industry produced concretes and the laboratory counterparts

5.9 Freeze-Thaw Scaling of Concretes Containing Different Fly Ashes

This section of the research project looked at how the various characteristics of the fly ash (fineness, L.O.I. and particle size) affects the durability during freeze-thaw including how well the air entrainer protects the concrete. All the concretes tested with fly ash cement all had a total replacement content of 35% in accordance with BS8500 concretes for freeze-thaw and with a target strength of 40MPa.

Figure 5.32 shows the freeze-thaw scaling results for both the air entrained and non-air entrained samples and Table 5.11 details the rate of deterioration and scaling rating to SS 137244. As observed, the non-air entrained samples fall into the unacceptable category when subjected to freeze-thaw testing. DFA2 performed well acquiring a *Good* scaling resistance which is odd because the fly ash characteristics from Table 3.1 shows that the fly ashes are similar in regard to their chemical composition. This means that there is a couple of possibilities that could influence the performance. Either the sealant was not secured enough to the concrete or another factor prevented the samples deteriorating such as a characteristic.

The former would be the choice as problems like this have already happened in other testing, however, these samples were constantly tested for leakage and these were sealed up tight. This means that there is another factor which is preventing the material from degrading.

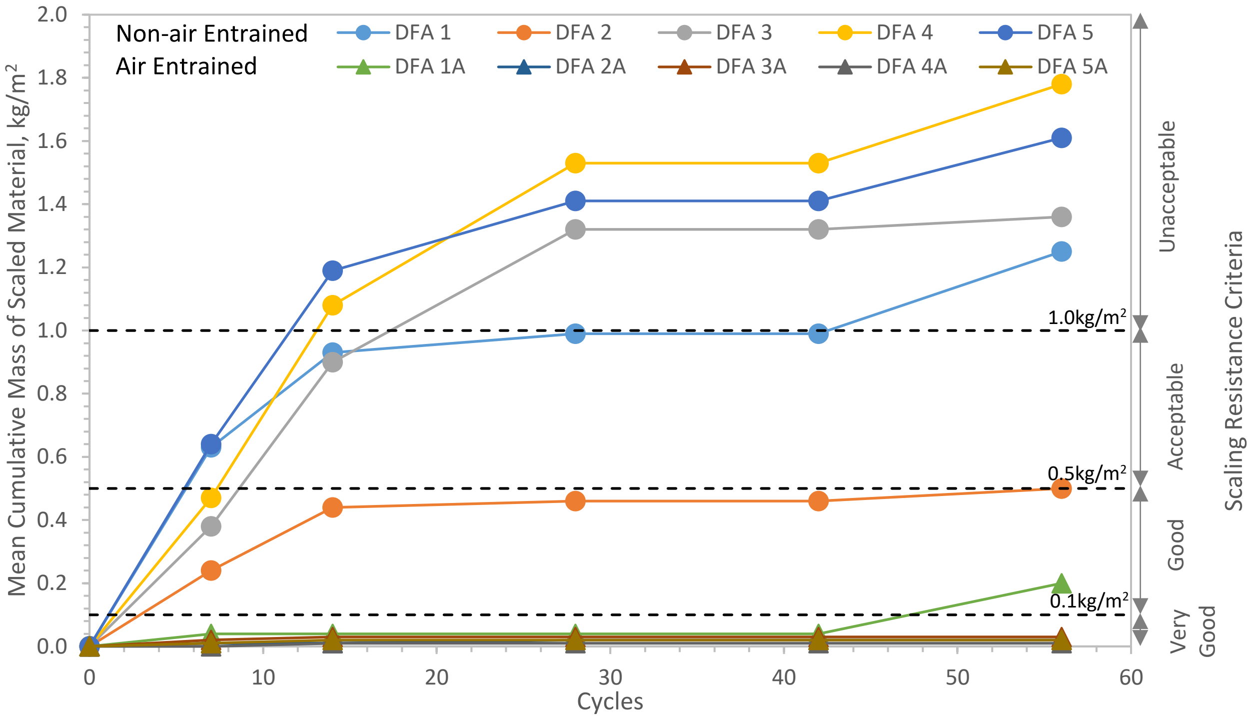


Figure 5.32 Freeze-thaw scaling of concrete containing different fly ashes with different properties and the scaling resistance criterion detailed in SS 137244

Table 5.11 Scaling criteria results for concretes containing different fly ash types with approximate cycle of unacceptable damage and the equation for the rate of deterioration

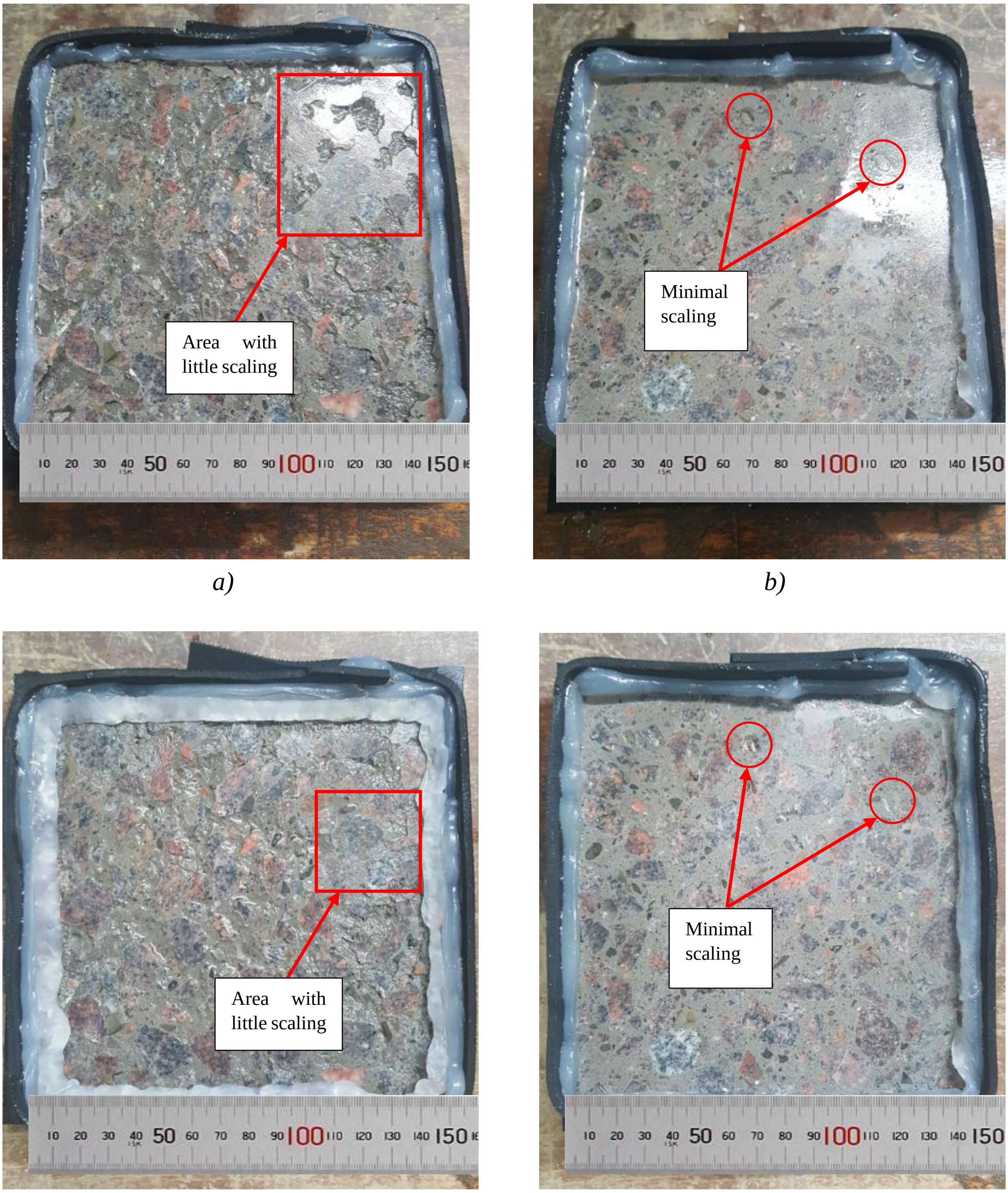
Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0 kg/m^2$	Sn_{56}/Sn_{28}	Rate of Deterioration, kg/m^2/cycle	Scaling Criteria
	L.O.I, %	Fineness	Air Content, %					
Non-Air Entrained								
DFA1/ M15	5.1	10.5	1.5	1.25	28 – 42	1.26	0.2415ln(x)	Unacceptable
DFA2	4.1	8.1	1.5	0.5	na	1.09	0.1077ln(x)	Good
DFA3	4.6	18.7	1.2	1.36	14 – 28	1.03	0.4775ln(x)	Unacceptable
DFA4	5.3	21.2	1.1	1.78	7 – 14	1.16	0.5981ln(x)	Unacceptable
DFA5	5.2	25.3	1.2	1.61	7 – 14	1.14	0.4216ln(x)	Unacceptable
Air Entrained								
DFA1A/ M20	5.1	10.5	4.7	0.2	na	5.0	0.0498ln(x)	Good
DFA2A	4.1	8.1	4.9	0.02	na	1.0	0.0059ln(x)	Very Good
DFA3A	4.6	18.7	4.4	0.03	na	1.0	0.0042ln(x)	Very Good
DFA4A	5.3	21.2	4.6	0.01	na	1.0	0.0042ln(x)	Very Good
DFA5A	5.2	25.3	4.7	0.02	na	1.0	0.0042ln(x)	Very Good

na – not applicable

Compressive strength is dependent on several properties particularly the cement type and the replacement percentage but also the type of admixture used. When it comes to entraining air into fly ash concretes there is a requirement that the amount used is significantly increased to accommodate the absorption by the fly ash particles. The addition of the extra air entrainer means that the water/cement ratio must be reduced to maintain the strength level whilst achieving the target air content. Figure 5.33 shows a visual comparison between air and non-air entrained CEM II/B-V concrete for 7 cycles and 56 cycles and Figure 5.34 shows the compressive strengths of the concretes compared against the freeze-thaw scaling results.

As the results show there is a distinct difference regarding the use of air entrainment for the compressive strength in freeze-thaw situations. Although the mix design has been altered to achieve a target strength with the air entrainer, the compressive strengths are slightly less for the air entrained concrete. Although, without air entrainment the CEM II/B-V concretes were not capable to withstand freeze-thaw. There are several parameters which define which fly ash is used in each situation and when it comes to freeze-thaw using category type S is the preferred option. There is a large difference in the fly ash scaling results regarding the category of fly ash used in the concrete. DFA1 and DFA2 are both category S meaning that they can withstand freeze-thaw conditions whereas category N fly ashes did not perform as well. Even with the reduced strengths the freeze-thaw resistance of the concretes is significantly increased showing that even poorer fly ashes can perform well in freeze-thaw provided enough air entrainer is used to maintain the target air content and the target strength is achieved or closely achieved.

What should be observed from the scaling results and the visual comparison is the amount of sealant used between 7 and 56 cycles. During the preparation stage of the freeze-thaw test, the black rubber wrap is attached to the sample using silicon sealant and then around the top of the sample is sealed to prevent any saline solution from leaking down the side. The freezing and thawing cycles cause the silicon sealant to contract and expand whilst still being attached to the concrete. This movement in the sealant causes the wrap to, in a way, perform mini pull out tests all around the sample resulting concrete to be pulled away and a space to open up and allowing the solution to pour off the top and making the freeze-thaw test ineffective. As shown from Figure 5.33, there was a noticeable difference in the amount of sealant around the top of the sample. In order to stop water leaking down the side, further application of the silicon is needed but due to the number of cracks appearing around the top more sealant is required to plug the leaks reducing the test surface area. A reduced surface area then reduces total mass of scaled material severally affecting the result, potentially implying that the concrete would pass the result when in fact it only passed due to the continual loss of the solution.



c) d)

Figure 5.33 Visual comparison between CEM II/B-V a) non-air entrained and b) air entrained concretes after 7 cycles c) non-air entrained and d) air entrained concretes after 56 cycles

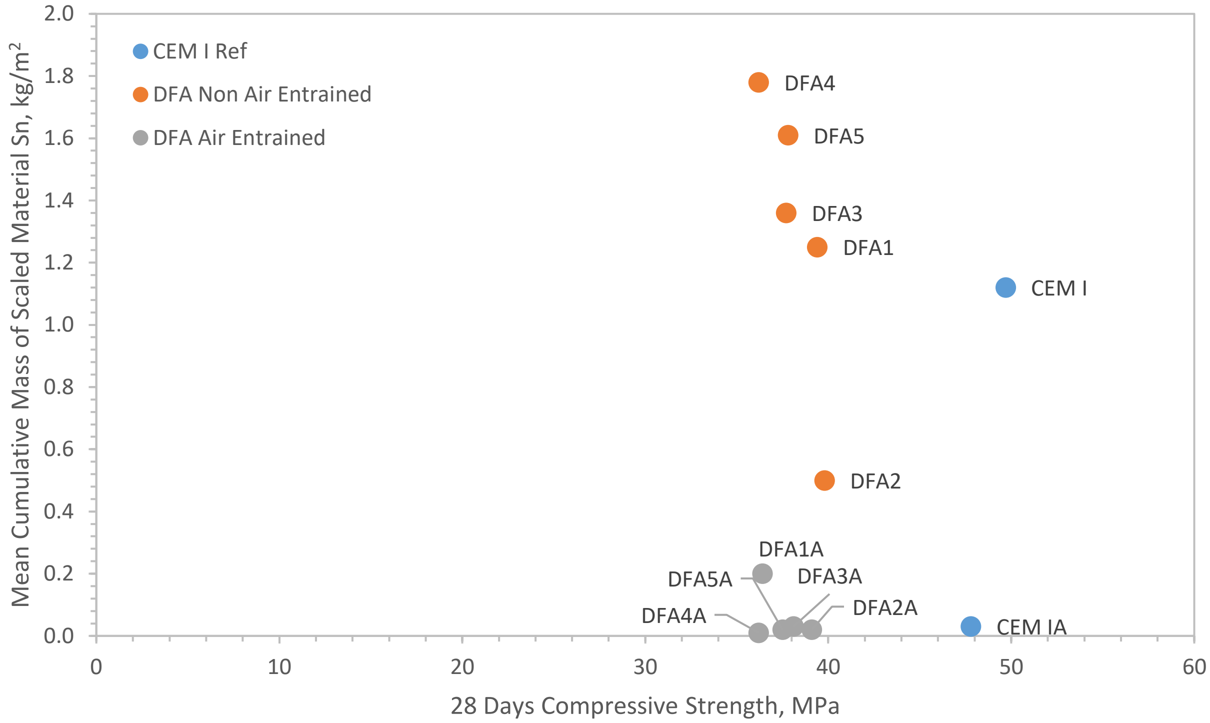


Figure 5.34 Compressive strength plotted against freeze-thaw scaling data for CEM I reference mixes and DFA non air and air entrained mixes

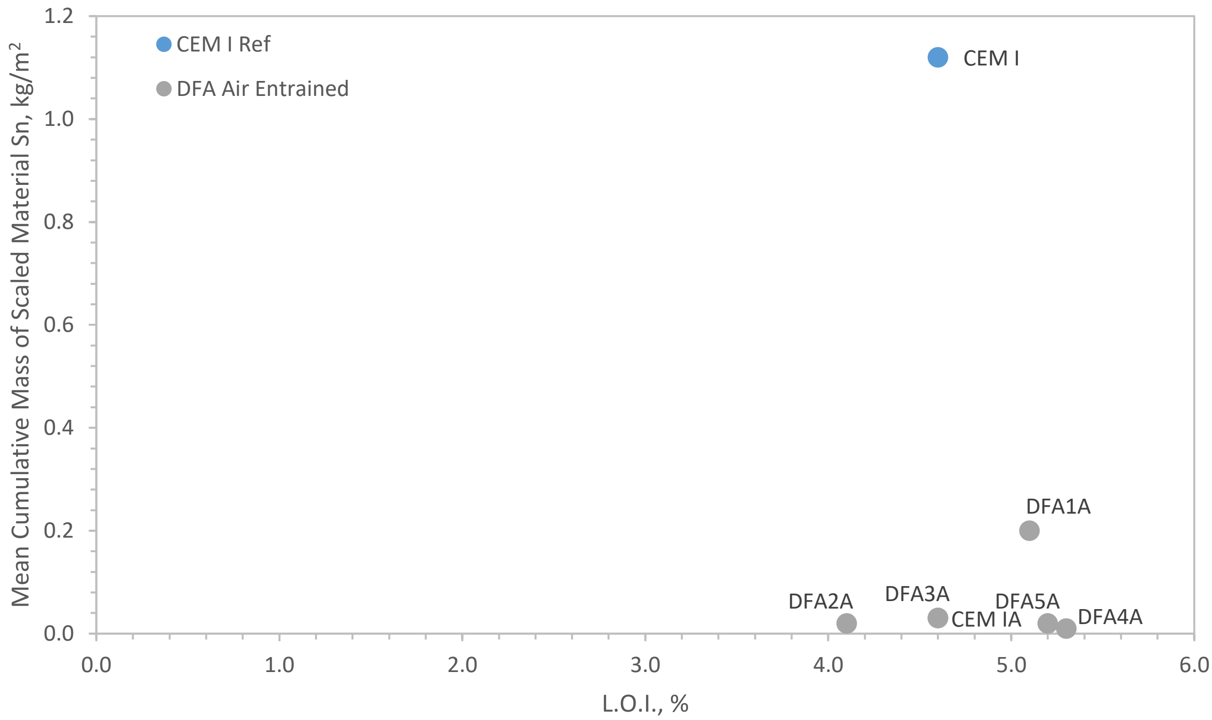


Figure 5.35 L.O.I. plotted against freeze-thaw scaling data for CEM I reference mixes and DFA air entrained mixes

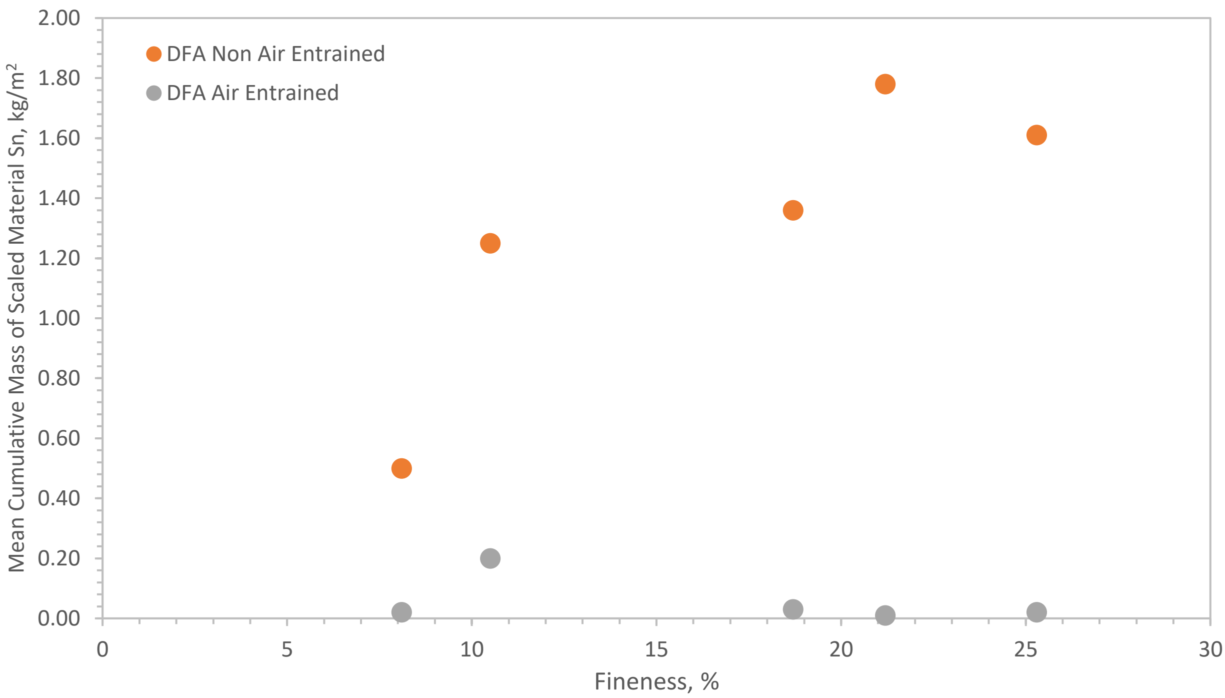


Figure 5.36 Fineness plotted against freeze-thaw scaling data for CEM I reference mixes and DFA non air and air entrained mixes

Looking at the physical characteristics of the different fly ashes, there is not any major differences in the characteristics. Figure 5.35 shows the L.O.I for each of the fly ashes used compared to the total amount of scaled material for the air entrained concretes. DFA2A does have a lower L.O.I. compared to the rest which suggests that the concrete performed better with the lower carbon percentage, but this value is 0.5% less than DFA3A (4.6%) which was given an *Unacceptable* rating for the scaling resistance (1.36 kg/m^2). L.O.I defines the total percentage of carbon in the ash and it is this left-over carbon which absorbs air entrainer. As shown the higher carbon content causes an increase in the scaling resulting in more material lost implying that with the removal of the carbon particles, or in larger particles, the fly ash should have a higher durability compared to the higher carbon content ashes. Figure 5.36 shows the comparison between the loss of material due to scaling and fineness of the ashes used.

The figure shows a significant decrease in the scaling of the concrete whether that be air or non-air entrained. This means despite the concrete still achieving an *Unacceptable* rating in accordance with SS137244, the durability of the concrete can be potentially increased if not only the ash was to be air entrained but with the removal of most of the carbon. This ties in with the work looking at the effects of the particle size of the material. With carbon particles in the concrete there are large voids in the concrete that need to be fill otherwise it leaves the concrete exposed for water to infiltrate into these voids, freeze, then exert pressure on the pore walls causing cracking. If most of the carbon is removed by re-burning, it leaves much smaller ash particles reducing the amount of scaling seen in Figure 5.35 and Figure 5.36.

5.10 Freeze-Thaw Scaling of Concretes with Different Admixture Combinations

The use of admixtures in concrete is a necessity to acquire the right properties needed for individual situations. The problem with using admixtures in concrete is that each cement type reacts differently when admixtures are added, and this can upset the design parameters. It is assumed that the admixtures used in the concreting sector are suitable for the various different cement types that are available on the market, however, this is not the case and generally the admixtures used in industry only target CEM I characteristics rather than the total cement content including the replacement material. Recently, admixture producers have designed several admixtures which also target different cements other than CEM I but are not widely used and most concrete producers stick to the CEM I admixtures.

Since there is an EU agenda for more sustainable options regarding concrete, less CEM I concrete is being produced and other concrete types are being implemented in a bid to reduce the CO2 emissions from the construction industry. In doing so, this section of the project looks at the freeze-thaw scaling of various admixture combinations to identify whether the interaction between different types of admixture and the cement paste benefits/hinders the overall performance. Furthermore, the various combinations were cast into CEM I concrete (control mix) and CEM III/A concrete for a comparison between different cement types.

Figure 5.37 shows the freeze-thaw scaling results of the different admixture combinations used and Table 5.12 details the combinations tested, mix characteristics, the numerical values for the test at 56 cycles, the rate of deterioration and the resistance criterion.

As seen in Figure 5.37, all mixes achieve a minimum acceptable scaling rating for having a total mass loss below 1.0 kg/m^2. It is observed that there are two mixes, AC1 (CEM I control) and AC4 (SP2 only), which lie above the 0.5kg/m^2 line. It is understandable that without any admixture the concrete would perform poorly during freeze-thaw as the fresh air content would be from entrapped air and not enough to improve performance. However, AC2 (CEM III/A control) which also did not have any admixture performed better with a decrease in the mass loss of 43% compared to AC1. This suggests that without admixture, CEM III/A concretes perform better than CEM I in freeze-thaw situations when the strengths are the same.

For AC4, the increase in deterioration compared to its counterpart AC3 (SP1 only) would be a result of the superplasticizer used for the workability. Some superplasticizers have a secondary benefit of being an air entrainer where additional air is added to the mix. Even though SP2 supplied more air than SP1, the conclusion is that SP2 did not have the ability to stabilize the microbubbles during the hydration process leading to coalescence or bleeding of the microair bubbles during compaction. AC8, AC9 and AC10 all have a good scaling rating as each of these mixes have superplasticizer and air entrainer which show that with increasing the workability of the concrete will allow the air entrainer of stabilize the microair structure more easily reducing freeze-thaw deterioration.

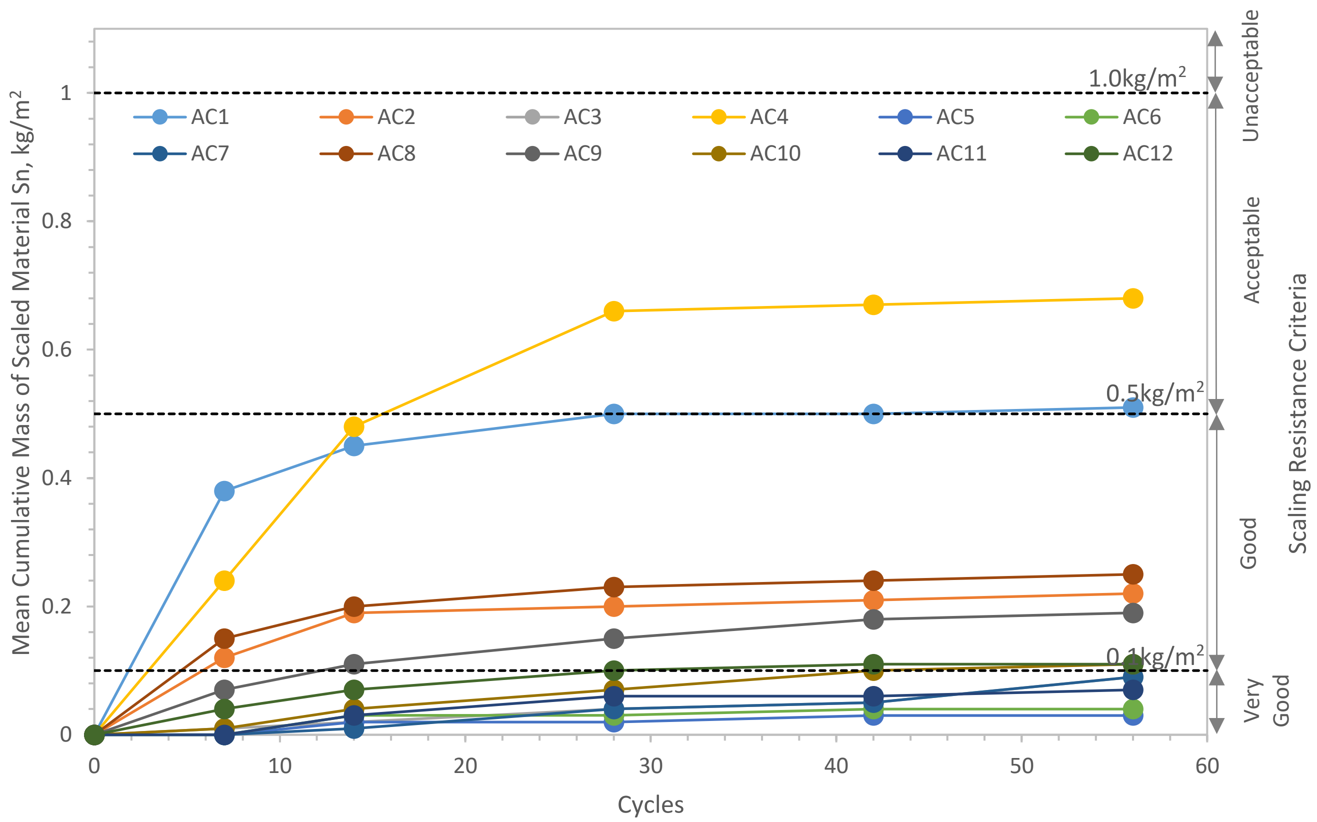


Figure 5.37 Freeze-thaw scaling of concrete containing different admixture combinations and the scaling resistance criterion detailed in SS 137244

Table 5.12 Scaling criteria results for concretes containing different admixtures with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics				Sn_{56}, kg/m²	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m²	Sn_{56}/Sn_{28}	Rate of Deterioration, kg/m²/cycle	Scaling Criteria
	Concrete Type	Admixture Combination	w/c	Air Content, %					
AC1	CEM I	No Adm	0.54	0.8	0.51	na	1.02	0.0618ln(x)	Acceptable
AC2	CEM III/A	No Adm	0.52	1.0	0.22	na	1.10	0.0434ln(x)	Good
AC3	CEM III/A	SP1	0.52	1.4	0.09	na	2.25	0.0337ln(x)	Very Good
AC4	CEM III/A	SP2	0.52	2.0	0.68	na	1.03	0.2148ln(x)	Acceptable
AC5	CEM III/A	AE1	0.44	4.6	0.03	na	1.50	0.0136ln(x)	Very Good
AC6	CEM III/A	AE2	0.44	4.0	0.04	na	1.33	0.0177ln(x)	Very Good
AC7	CEM III/A	SP1 + AE1	0.44	4.7	0.09	na	2.25	0.0396ln(x)	Very Good
AC8	CEM III/A	SP1 + AE2	0.44	4.2	0.25	na	1.09	0.0469ln(x)	Good
AC9	CEM III/A	SP2 + AE1	0.44	4.7	0.19	na	1.27	0.0591ln(x)	Good
AC10	CEM III/A	SP2 + AE2	0.44	4.2	0.11	na	1.57	0.049ln(x)	Good
AC11	CEM III/A	ACC + AE1	0.44	4.4	0.07	na	1.17	0.0334ln(x)	Very Good
AC12	CEM III/A	VMA + AE1	0.44	4.4	0.11	na	1.10	0.0355ln(x)	Good

na – not applicable

AC3 is observed to have very good scaling resistance with only superplasticizer which suggests that there is no requirement for air entrainer to be added when using CEM III/A concrete. This coincides with previous work done (Bijen, 1996) stating the air entrainer provides little added protection for freeze-thaw. It is noticed that AC4 (which also only has superplasticizer) manages to only achieve an acceptable scaling rating meaning that it is not just superplasticizer used but the type also.

Even though previous research has led to the conclusion that air entrainer is not required, and the current results stipulate the same outcomes, it should be considered that air entrainer does provide some sort of protection. AC5 and AC6 both have different types of air entrainer yet target air contents are reached and durability in freeze-thaw is very good, similar results shown for AC3. Comparing AC3, AC4, AC5 and AC6 to AC2, there is an indication that using either air entrainer or superplasticizer in a CEM III/A concrete would improve the overall performance of the concrete. This would mean that because of the nature of the admixtures (both having a main purpose and having a side benefit of the other) using either one in a CEM III/A concrete for freeze-thaw would provide enough protection so that minimum scaling occurs.

AC11 is shown to have very good freeze-thaw durability compared other mixes with both air entrainer and superplasticizer. Aside from AC7, AC11 performs much better than AC8, AC9 and AC10 which all contain admixtures designed to improve the durability against freeze-thaw. The addition of an accelerator may have benefited in the performance of the concrete rather than a superplasticizer. As the name suggests, an accelerator increases the rate of hydration to produce an early high strength which would have rapidly increased the stabilization of the microair bubbles preventing bubble loss.

Viscosity modifying admixtures (VMA) are a relatively new admixture designed to reduce segregation and bleeding of water and fines in the concrete. Generally used for self-compacting and underwater concretes to prevent the problems listed above, the admixture provides several side benefits for the durability. A VMA was used in AC12 combined with air entrainer to determine their compatibility. From Table 5.12, it is identified that using a VMA in the concrete for freeze-thaw improves the performance. One of the side benefits of the VMA is the admixtures the ‘lubricating effect’ whereby water and fines are homogeneously controlled creating a coating around the coarse aggregate decreasing frictional forces and increasing pumping power. If this coating were present during the mixing of the concrete then it would result in a reduction of the microair bubbles lost, thus providing the necessary protection for freeze-thaw attack.

5.11 Summary of Chapter 5

This chapter has looked at, in depth, many different parameters which can influence the durability of concretes during freeze-thaw attack. Different concretes were analysed throughout the course of the chapter to understand how each of them react when freezing and thawing takes place for both air and non-air entrained samples and for a range of strengths for these concretes. The results of the testing identified that with the increase in the strength there is a reduction in the amount of scaled material lost.

However, from the studies carried out during this chapter it was not only identified but further encouraged the use of air entraining admixture in all concretes in freeze-thaw conditions because of the constant testing proving that the use of higher strength alone is not enough to ensure sufficient protection. CEM I saw 20, 30 and 40 MPa strength non-air entrained concretes pass the acceptable rating with the 50 MPa concrete barely achieving an acceptable showing that simple increasing the strength does not provide adequate protection for the concrete. Figure 5.38 shows a how different concrete properties influence the freeze-thaw resistance of concrete in the form of a triangle.

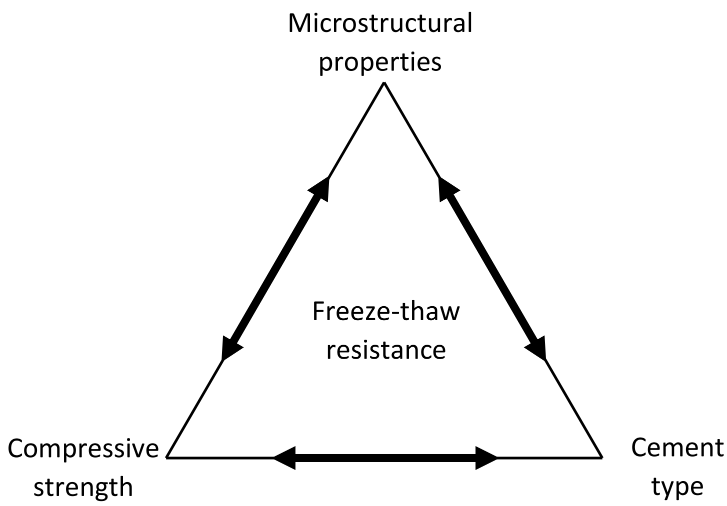


Figure 5.38 Relationship triangle showing how each of the factors that influence a concrete's freeze-thaw resistance

The influence of increasing the air content was studied to identify how much the increase in air entrainer not only reduced the total scaled material but how the increase influenced the concrete's microstructural properties and the knock-on effect to the air void parameters and strength. The benefit being that the higher air content would prevent scaling of the concrete but the hindrance being that it would seriously impact the concretes overall strength which, when enough strength is lost, the concrete would not be able to withstand freeze-thaw attack no matter how much air entrainer was in the mix. Moreover, the concretes with higher air entrainer quantities plateaued at particular points meaning that if more air entrainer was continually added to the concrete, it would result in the mix becoming more workable due to the admixture's side benefit of having superplasticizer qualities.

Higher replacement content concretes (above the maximum allowance as defined in BS8500) were tested on the freeze-thaw durability. The strength-scaling comparison shows an unusual distribution in the results whereby the lower strength CEM II/A-L performed better in freeze-thaw than the higher strength CEM II/B-V because of the particle size of the replacement materials. Furthermore, CEM III/A only saw a 15% drop in the strength for this highest replacement content of 85% and producing a very good scaling rating with material loss of 0.05kg/m^2. This also means that with a small amount of CEM I in the concrete CEM III/A concretes can be more sustainable and can be used in freeze-thaw conditions.

The microair content is a new parameter looking at the total cumulative air content of void sizes 300µm and less and by this definition a high microair content means a better freeze-thaw protection due to higher void count of smaller size. The problem with using the current definition of microair content is that it includes void sizes less than 30µm meaning that even with the extra voids it drastically increasing the total number of voids and reducing the spacing factor whilst being good because the air entrained voids are being distributed throughout the concrete, these sizes do not have the capacity to allow ice expansion to take place as they are too small.

The influence of using XF3 rated aggregates in concretes in XF4 conditions was tested to determine how much of a difference there would be regarding freeze-thaw scaling. Local gravel was used for comparison which is a porous material compared to crushed granite. The concrete mix designs were kept the same with the only difference being the coarse aggregate replaced with gravel. Changing the aggregates saw the XF4 (granite) aggregates outperform XF3 (gravel) aggregates but that was based upon the total mass loss of the overall concrete. Further investigation shows that the mass lost from the concretes containing gravel were not from the cement paste like the previous concretes but from the aggregate. Because the gravel is a porous material, the ice built up in the pores of the aggregate rather than the concrete pores to begin with, but with continuous freezing and thawing the aggregate does not meet durability requirements for freeze-thaw.

Utilising fly ash in concrete has aided in pushing European sustainability agendas for a long time and whist using fly ash has reduced CO_2 emissions from CEM I production it does come at a cost. Fly ash is the type of material which can be unpredictable from mix to mix despite the ash coming from the same stockpile or coal fired power plant. What is more problematic is when fly ash is used in concrete that is subjected to freeze-thaw. Typically, when concrete is subjected to freeze-thaw the strength is increased and air entrainer is added to prevent cracking, however, fly ash concretes absorbs the air entrainer requiring dosages up to three times the amount used in a CEM I concrete. Many different parameters were tested during this research project such as the category type (either type S or N), strength, fineness and carbon content.

Various admixture combinations were tested to identify whether the mixture of different admixture types influenced the microstructural properties of the concrete and therefore, the freeze-thaw resistance. As shown, combining air entraining admixture and superplasticizer are a common combination to achieve a good air content. What has not been considered is the use of an accelerator and a VMA in conjunction with air entrainer for concretes that require these admixture combinations. It was investigated and shown that even with these different combinations of four different admixtures, the freeze-thaw resistance was still maintained meaning that combining admixture does not deviate the air entrainer from protecting the concrete subjected to freeze-thaw attack.

From the results it is clear that there are several factors that have to be including higher addition percentages and the combination of different admixtures into a mix, especially now that admixtures tend to have secondary benefits. Moreover the standards have to reflect this so that concretes can be designed to consider the climate change, cement and admixture develop. Table 5.13 shows the Exposure Classes as defined in BS 8500 with the addition of XF5 to consider permanent saturation and prolonged exposure to freeze-thaw. Table 5.14 details the cement requirement for XF5 for future concrete design showing the minimum cement and contents, aggregate requirement and the higher than average quantity of de-icing salt the concrete may be exposed to.

Table 5.13 Freeze-thaw exposure class designation showing those detailed in BS EN 206-1 and BS 8500 with an additional row for an XF5 classification

Class Designation	Class Description	Informative Examples Applicable in the United Kingdom
XF1	Moderate water saturation without de-icing agent	Vertical concrete surfaces such as facades and columns exposed to rain and freezing Non-vertical concrete surfaces not highly saturated, but exposed to freezing and rain or water
XF2	Moderate water saturation with de-icing agent	Concrete surfaces such as parts of bridges, which would otherwise be classified as XF1, but which are exposed to de-icing salts either directly or as spray or run-off
XF3	High water saturation without de-icing agent	Horizontal or near horizontal concrete surfaces, which are exposed to freezing whilst wet Concrete surfaces subjected to frequent splashing with water and exposed to freezing
XF4	High water saturation with de-icing agent or sea water	Horizontal concrete surfaces such as roads and pavements, exposed to freezing and to de-icing salts either directly or as spray or run-off Concrete surfaces subjected to frequent splashing with water containing de-icing agents exposed to freezing
XF5	*Permanent saturation with continuous prolonged exposure to de-icing agent or sea water*	*Horizontal concrete surfaces such as roads and pavements, exposed to freezing and to de-icing salts continuously either directly or as spray or run-off* *Concrete surfaces subjected to constant splashing with water containing de-icing agents exposed to freezing*

Table 5.14 Limiting values for composition and properties of concrete to resist freezing and thawing for XF exposures with the addition for XF5 Exposure Class

Exposure Class	Min. Strength Class	Max. w/c ratio	Min. air content (%) and min. cement or combination content (kg/m³) for max. aggregate size				Other requirements	Cement and combinations
			32 mm or 40 mm	20 mm	14 mm	10 mm		
XF1	C25/30	0.60	4.0	4.5	5.5	6.5	-	See[1]
			260	280	300	320		
	C28/35	0.60	-	-	-	-		
	LC28/31		260	280	300	320		
XF2	C25/30	0.60	4.0	4.5	5.5	6.5	-	See[1]
			260	280	300	320		
	C32/40	0.55	-	-	-	-		
	LC32/35		280	300	320	340		
XF3	C25/30	0.60	4.0	4.5	5.5	6.5	Freeze-thaw resisting aggregates[3]	See[2]
			260	280	300	320		
	C40/50	0.45	-	-	-	-		
	LC40/44		320	340	360	360		
XF4	C28/35	0.55	4.0	4.5	5.5	6.5	Freeze-thaw resisting aggregates[3]	See[2]
			280	300	320	340		
	C40/50	0.45	-	-	-	-		
	LC40/44		320	340	360	360		
XF5	*C32/40*	*0.55*	*4.0*	*4.5*	*5.5*	*6.5*	*Freeze-thaw resisting aggregates*[3]	*See*[2]
			300	*320*	*340*	*360*		
	C40/50	*0.42*	-	-	-	-	*High coverage rate for de-icing salt*[4]	
			320	*340*	*360*	*380*		
	LC40/44	*0.40*	*360*	*380*	*400*	*420*		

(1) CEM I, II/A-D, II/A-L, II/A-LL, II/A-S, II/B-S, II/A-V, II/B-V, III/A, III/B, IVB-V

(2) IVB-V is not used for XF3/4 as the limiting factors for fly ash and GGBS is 35% and 55% respectively

(3) In accordance with EN 12620

(4) Coverage rate based upon 6-9% salt concentration from CEN/TS 12390-9 and guidance from the Scottish Government on average coverage between 170 – 270 g/m^2.

Chapter 6
Influence of Lightweight Aggregate Concrete Subjected to Freeze-Thaw Conditions

6.1 Introduction

Sustainability agendas put forward by the EU not only look at reducing the CO_2 emissions caused by cement production but the concrete industry. Currently, the use of replacement materials such as fly ash and GGBS are common instead of CEM I but it is not just the cement which is being replaced. Aggregates are now having a certain percentage of material replaced with recycled concrete or crushed masonry to reduce waste and CO_2 emissions that would otherwise be produced from quarrying or mining.

In Chapter 5, a brief comparison was done between XF and non-XF compliant aggregates and deteriorations seen between them. This chapter looks at how using lightweight aggregate in concrete influences the concrete's hardened properties such as the air content and resistance to freeze-thaw attack. BS 8500 states different concrete designs can be used to resist specific exposure classes of different environmental conditions. According to BS 8500, using a C28/35 air entrained concrete has the equivalent freeze-thaw resistance (XF4 exposure class) as C40/50 non-air entrained. Furthermore, BS 8500 states lightweight aggregate can be used. This concrete ranges between the normal weight air entrained concrete and non-air entrained high strength concrete on the list of possible concrete mixes, only difference is that lightweight aggregate concrete does not have a high strength, nor does it contain air entraining admixture. This suggests that the lightweight aggregate has the potential to resist freeze-thaw attack in a similar way that air entrainment does.

To understand how the aggregate, provide said protection, a series of tests were carried out including two different freeze-thaw test methods for aggregates to identify the aggregates ability to withstand freeze-thaw conditions. Other quantitative analysis including micro-CT porosity and mercury intrusion porosity (MIP) looked at the microstructural properties of the aggregate and analysis was conducted on the concrete to determine how the aggregate influences the air void system.

6.2 Influence of Lightweight Aggregate on the Hardened Concrete Properties (Phase 1c)

The use of lightweight aggregate is used in concrete to reduce the concretes density, thus, the self-weight. Typically, when a concrete uses normal aggregate, two different size ranges are used (4-10mm and 10-20mm) for the coarse aggregate whilst for lightweight aggregate, when used in industry, the size range is between 4-14mm (although other sizes are available on request). Lightweight aggregate is produced using the sintering process where damp fly ash is placed into large rotating pelletizers to form the aggregate pellets. The aggregate is limited to 14mm diameter as anything larger would not be strong enough to withstand the sintering process where the temperature reaches 1100°C before being mechanically graded (Sasha, 1999).

Three groups of concretes were cast for comparison looking at the hardened properties and how the use of lightweight aggregates can influence the air void characteristics and freeze-thaw scaling resistance. Control mix concretes which had a designated strength outlined in BS 8500. LWA1-LWA3 concretes with lightweight aggregate and natural glacial sand. LWA4-LWA6 was the same as LWA1-LWA3 only lightweight sand was used. Table 6.1 details the concretes used for the study and the differences between.

Table 6.1 Concretes used during the lightweight aggregate study

Mix Code		**Designated Strength, MPa**	**Description**
Control Mix	C1	C28/35	Control CEM III/A concrete with no air entrainer used as a comparison to air entrained concrete
	C2	C28/35 with air	Control CEM III/A concrete with air entrainer as detailed in BS8500 for comparison with lightweight aggregate concrete
	C3	RC40/50	BS8500 specified CEM III/A concrete for freeze-thaw resistance without air entrainer
Using natural glacial sand	LWA1	LC40/44	CEM I concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with natural glacial sand
	LWA2	LC40/44	CEM III/A concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with natural glacial sand
	LWA3	LC40/44 with Cl	CEM III/A concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with natural glacial sand purposely added chloride salt
Using lightweight sand	LWA4	LC40/44	CEM I concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with lightweight sand
	LWA5	LC40/44	CEM III/A concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with lightweight sand
	LWA6	LC40/44 with Cl	CEM III/A concrete containing lightweight aggregate not requiring air entrainer for freeze-thaw with lightweight sand purposely added chloride salt

LWA3 and LWA6 had sodium chloride salt included in the mix to determine is the inclusion of salt in the mix affects the performance of the concrete during freeze-thaw because it was suggested (by the author) that one of the reasons why the concrete performs well was that the lightweight aggregate stores salt particles in the pores.

6.2.1 Influence of Lightweight Aggregate on the Compressive Strength Development

Aggregates play a large part in the compressive strength of concrete. If a concrete has an aggregate which is porous then it can be just as weak as an air entrained concrete with no adjustment to the cement content to achieve the target strength. Lightweight aggregate is an unusual material when it comes to testing because of the microstructural properties and the size of the material. In Chapter 5, it was discussed that gravel does not perform as well as granite because of how porous the material is. The material reduces the concretes compressive strength because there are many voids in the 20mm aggregate. Figure 6.1 shows the compressive strength development of the three sets of concretes

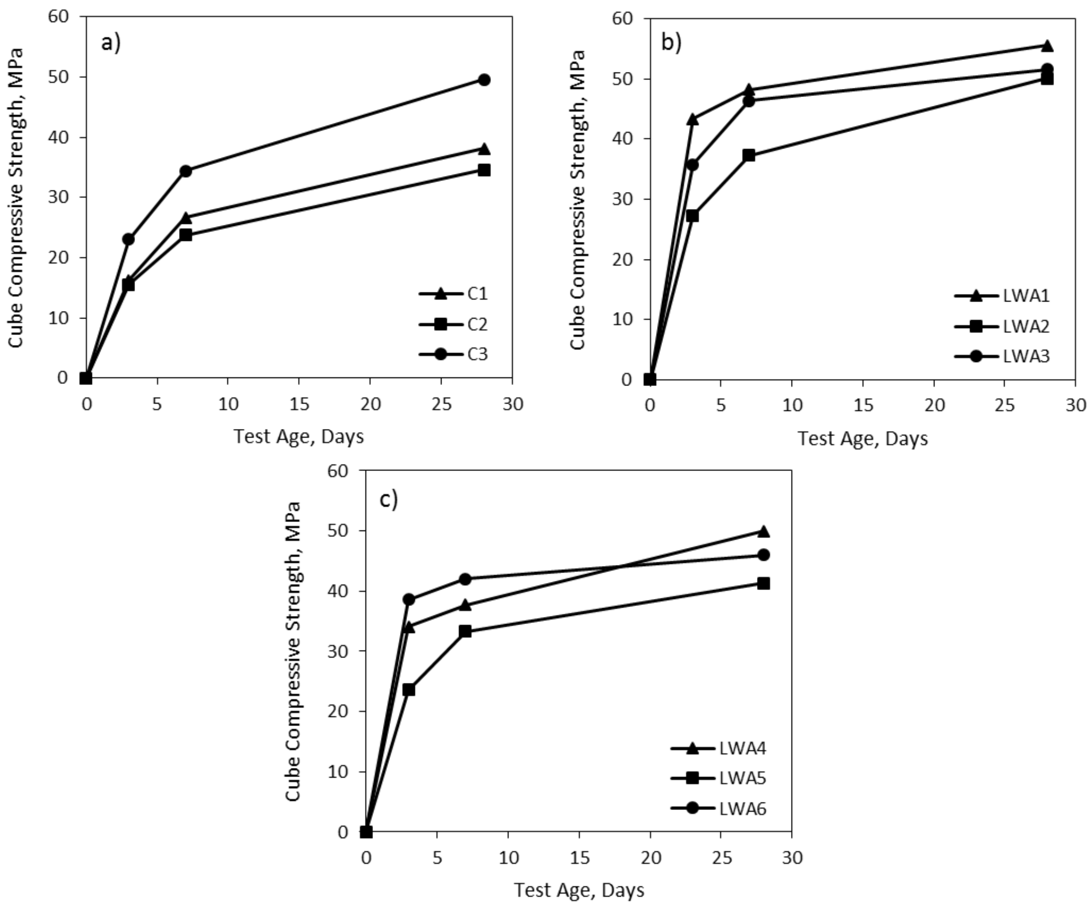


Figure 6.1 Compressive strength development of a) control concretes, b) concretes containing lightweight coarse aggregates and c) concretes containing lightweight coarse and fine aggregates

Lightweight aggregate is similar in structure to gravel as there are many voids within the aggregate with the difference being that for the lightweight the voids are much smaller but are distributed thoroughly throughout the concrete. What is unusual about this is when a concrete has a lot of voids it reduces the compressive strength, however, the compressive strength of the lightweight aggregate concrete is higher in the first 3–7 days compared to the control concretes during the same period. Moreover, once the concretes reach 28 days the compressive strength of LWA2 and LWA3 (with natural glacial sand as a fine aggregate) are higher than C3 (RC40/50) despite there being a porous aggregate in LWA concretes and Control concretes using granite. Though LWA4 – LWA6 do not have as a high strength as C3, they still have a higher strength than C1 and C2.

A reason behind the compressive strength being higher for the lightweight aggregate would be the specification of the amount of aggregate to use pre-mix. Normally a concrete would have smaller and larger aggregates which are determined and make up the total density. For example, control mix C1 has a total of 1110kg/m^3 (370kg/m^3 of 4/10mm and 740kg/m^3 of 10/20mm aggregate) whereas lightweight coarse aggregate (6/14mm) only specifies 759kg/m^3 for LWA1. Comparing the difference in coarse aggregate contents, control mix C1 total coarse aggregate content is 47% of the total content (2363kg/m^3) whereas the content is 41% for lightweight showing there is not a big difference in the contents. The slight increase in the compressive strength for the lightweight aggregate concrete can be attributed to this reduction in the total coarse aggregate content. Table 6.2 shows a comparison between a conventional normal weight concrete to lightweight aggregate concrete.

Table 6.2 Comparison between aggregate/cement ratios for a 40 MPa normal and lightweight aggregate concretes

Concrete Aggregate Type	**Cement/Aggregate Ratio**
Normal aggregate (granite)	0.21
Lightweight aggregate	0.38

6.2.2 Influence of Lightweight Aggregate on the Air Void System

Chapter 4 discussed how the physical properties such as the cement type, target strength, air entrainer influence and replacement content percentage for a different concrete affects the microstructural characteristics in the concrete. Lightweight aggregate has similar results to gravel concretes whereby due to the porosity of the aggregate it increases the total air content because of the extra pores which are picked up by the air void analyser. As with the samples in Chapter 4, the lightweight concretes were polished to produce a smooth surface for the analyser to read the voids from. The results for the air contents for the fresh and hardened states are shown in Figure 6.2.

As the figure shows most of the concretes sit on or close to the line of equality showing a good correlation between the fresh and hardened states. Apart from control mix C2 (C28/35 air entrained as described in BS 8500) all the concretes sit either on the line of equality or above it is stating that the concretes have a higher air content in the hardened state rather than the fresh.

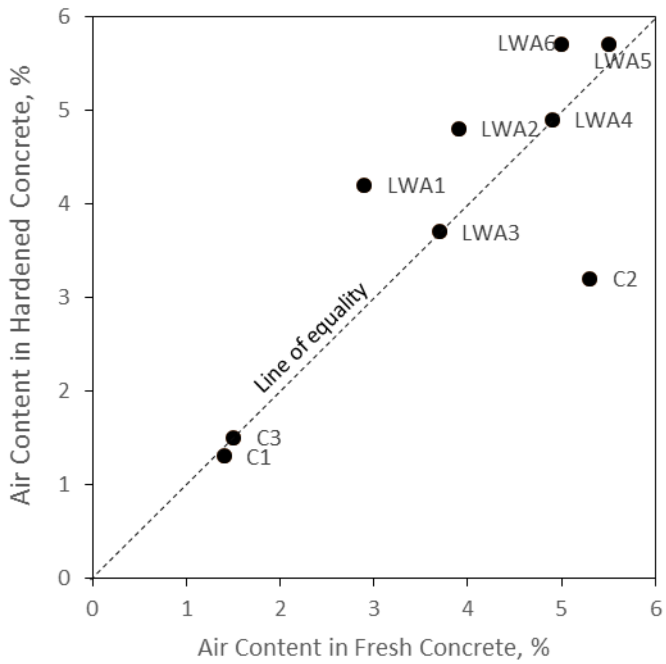


Figure 6.2 Comparison of air content measured in fresh and hardened concrete for control series (C1-C3), lightweight coarse aggregates (LWA1-LWA3) and lightweight coarse and fine aggregate (LWA4-LWA6) concretes

This correlates with the lightweight aggregate being saturated in water 24 hours before which minimises the volume of air in the aggregate and reduces the amount of free water the aggregate absorbs during the mixing and curing processes. The saturation of the aggregates decreases the volume of air in the aggregate's voids meaning that when the air content of a concrete is tested, the air content meter determines the air content in the concrete only.

In theory this would apply to the lightweight aggregate, however, there is no way to guarantee the aggregate is fully saturated nor is there a method to determine if the concrete is fully saturated. A test was undertaken to determine if there was a difference between the water absorption of a vacuum sealed sample and a sample stored in water for 24 hours. The results showed the vacuum sealed sample absorbed an additional 1.4% water than the material stored for 24 hours indicating that storing the material in water is very close to fully saturated when mixed with concrete meaning minimal free water would be absorbed by the lightweight aggregate.

On the other hand, when the hardened concrete is analysed the air content increases by comparison because of the exposed voids can be fully analysed. With the voids exposed, the analyser can determine the characteristics such as the air content and not be constrained by with the assumption that the aggregate is fully saturated meaning that even though the concrete is saturated in water for a period of time, and it is assumed that there is very little air in the aggregate, when the concrete is mixed the aggregate will not absorb any of the free water.

Although it was assumed the aggregate was fully saturated, there was still air in the concretes particularly in the concretes containing lightweight aggregate. As shown in Figure 6.2, there was still residual air in either the aggregate or in the concrete from entrapped air. With the assumed full saturation of the aggregate, the figure shows a high air content which would provide the concrete with adequate protection against freeze-thaw attack. Moreover, unless the aggregates used in the concrete are XF4 (for example granite) where the material has very little porosity, then the air content for the hardened state will always be higher than the fresh state. Table 6.3 shows the air void characteristics of the concretes used for the lightweight study determined by the air void analyser.

Table 6.3 Air void characteristics of the concretes used for the lightweight aggregate study

Mix Code	Air Content, %		Spacing Factor, mm	Specific Surface, mm^{-1}	Void Frequency, mm^{-1}	Average Chord Length, mm	Microair Content, %
	Fresh State	Hardened State					
C1	1.4	1.36	0.106	61.30	0.502	0.070	2.12
C2	5.3	3.22	0.167	33.55	0.270	0.121	2.00
C3	1.5	1.54	0.205	43.19	0.167	0.093	0.95
LWA1	2.9	4.27	0.082	47.97	0.632	0.085	4.30
LWA2	3.9	4.84	0.086	50.36	0.607	0.080	3.66
LWA3	3.7	3.69	0.119	42.15	0.390	0.095	2.99
LWA4	4.9	5.25	0.058	57.71	0.756	0.070	4.46
LWA5	5.5	5.71	0.058	56.66	0.814	0.071	4.92
LWA6	5.0	5.66	0.065	50.96	0.721	0.079	4.23

6.2.3 Effect of Lightweight Aggregate on the Microair Air Void Parameter

In Chapter 5, it was discussed that the microair content changes how the other air void characteristics are calculated because of the size range. The problem with using the microair content is that it is a fraction of the total air content to a certain size range meaning that there is not much to differentiate it from the total air content determined apart from a 'cut off' point in terms of the size range.

The results in Figure 6.3 show the microair content (<300μm) as a percentage of the total air content (<4000μm). Aside from the fact that two out of the three control mixes do not have air entrainment, there is still air in the concrete that makes up a large percentage of the total air content. From the figure, the lightweight mixes (LWA1-6) show a high microair content with the lowest value being 75% of the total air content. This illustrates that due to the size of the voids in the aggregate the microair content will always constitute the majority of the total air content. It has been shown that newly developed air entrainers are produced in such a way that they form micro-voids in the concrete, keeping the total air content relatively similar but increasing the number of voids.

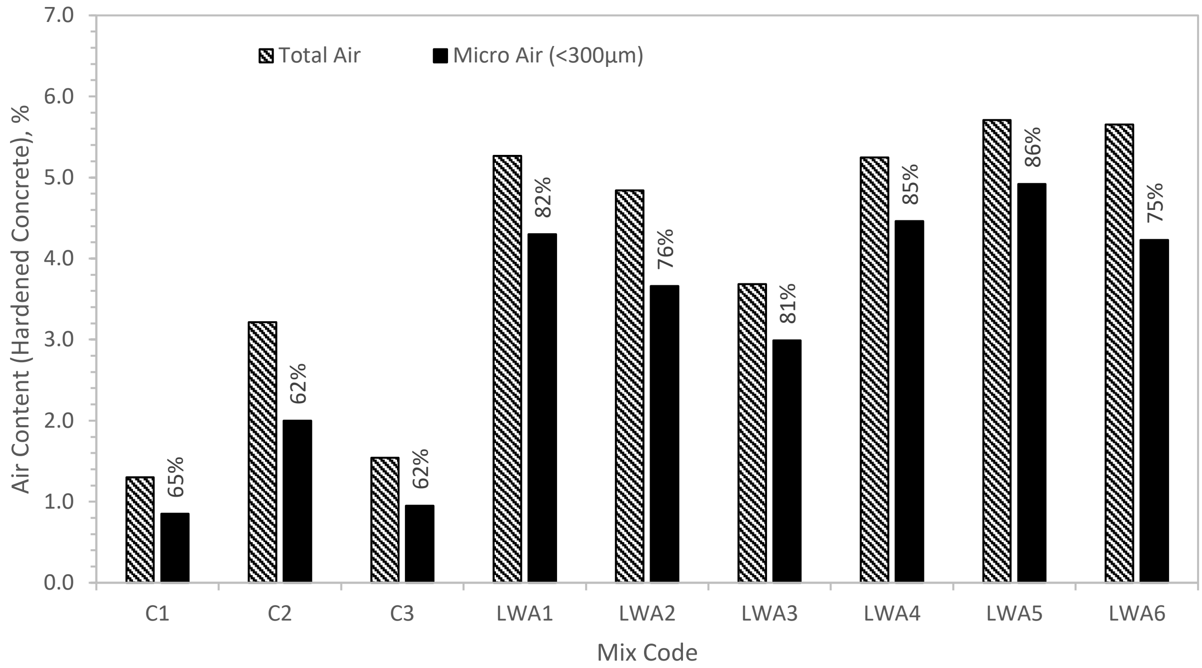


Figure 6.3 Comparison between the different concretes used in the study showing the microair content (<300µm) as a percentage of the total air content (<4000µm)

For lightweight concrete the principle is slightly different as there is no air entrainment but at the same time the microair content is just as high as it would be if the concrete contained normal freeze-thaw resisting aggregates with air entrainment. In addition, the lightweight concretes tested in the study do have similar amount of superplasticizer compared to normal concrete, so the contributions are approximately the same. In order to show the similarities between an air entrained concrete and the lightweight aggregate concrete, Figure 6.4 shows a comparison between the number of voids distributed over different void sizes.

Though Figure 6.4 shows a similar trend between the air entrained normal weight concrete and the non-air entrained lightweight aggregate concrete, there is a possibility that statistically there is a difference in the results. Comparing an air entrained CEM III/A normal aggregate and a non-air entrained CEM III/A lightweight aggregate as these were of similar constituent consistence with only coarse aggregate changed, a *t-test'* was conducted on the results shown in Figure 6.4 showing that the probability of the data is random is 0.4% giving a confidence value of 99.6% meaning that the data is significantly different. Further analysis undertaken (Table 6.4) compared the other lightweight samples to C2 (air entrained CEM III/A normal aggregate concrete) and shown that there is a consistent result showing that all lightweight concretes have a similar trend to the air entrained normal aggregate concrete. LWA3 is shown to be an outlier with a random data value of 3% suggesting there was not a similar quantity of voids for an equal trend.

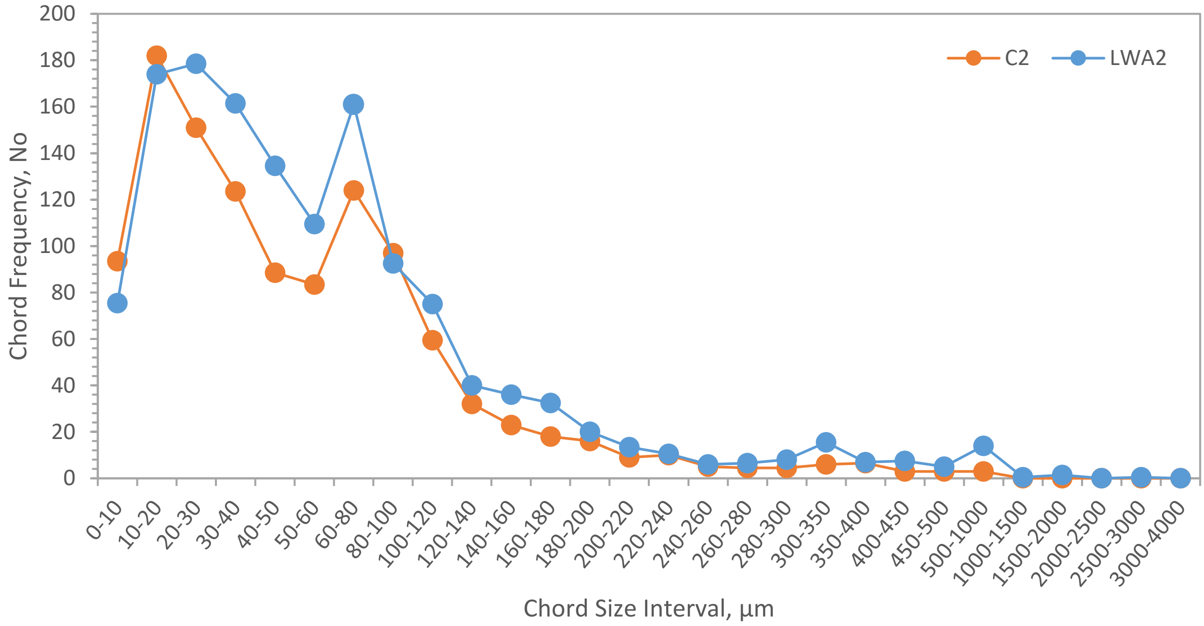


Figure 6.4 Comparison of the total number of voids counted in their respective size range between a CEM III/A air entrained concrete with freeze-thaw resisting aggregate and a CEM III/A non-air entrained concrete containing lightweight aggregate

Table 6.4 Comparison between t-test results from the air entrained CEM III/A normal aggregate and the lightweight aggregates concretes

Mix Code	Probability of Random Data, %	Confidence, %
LWA1	0.04	99.96
LWA2	0.40	99.60
LWA3	3.00	97.00
LWA4	0.02	99.98
LWA5	0.05	99.95
LWA6	0.02	99.98

6.3 Influence of Lightweight Aggregates on the Freeze-Thaw Durability of Concrete

Testing lightweight aggregate concretes is slightly different compared to normal concrete as they require more preparation. As discussed, lightweight aggregates are made from fly ash which is known to absorb admixture (depending on the quantity of unburnt carbon content), particularly air entrainer, during the mixing process thus needing a higher quantity. For lightweight aggregate it is not any different as the material absorbs a very high quantity of water.

With a high-water absorption, the aggregates were saturated in water in a non-vacuumed container for 24 hours at room temperature (20°C) and were then surface-dried before being used. This prevented the material from absorbing the free water during the mixing process. Moreover, had the extra 14% water been added during the mixing process there is no guarantee that the aggregate would absorb the water before hydration meaning there was a possibility that the extra would have increased the water/cement ratio and decreasing the compressive strength.

Figure 6.5 shows the freeze-thaw scaling results for the concretes tested in the lightweight study. Table 6.5 shows the rate of deterioration and the scaling rate criteria defined by SS 137244. From the figure it illustrates that using lightweight material is shown to improve a concrete's freeze-thaw resistance. Even with air entrainment being omitted from the mix, the concretes containing lightweight aggregate show to perform very well.

As previously stated, three groups of mixes were used for the study varying the fine and coarse aggregates between typical materials and lightweight materials. Whilst C1-C3 looked at different normal concretes used, LWA1–3 and LWA4–6 looked at using lightweight aggregate with natural sand for LWA1-3 and lightweight sand for LWA4-6 though these were not the only differences. Within LWA1-3 and LWA4–6 the cement types were varied between CEM I and CEM III/A but also had the addition of sodium chloride salt into one of the concretes in each set to determine if the aggregate was absorbing the salt which reduced the loss of scaled material.

Control mixes C1–C3 comprise the control mixes which were listed in BS 8500. C1 and C2 are the same mix design with C2 being air entrained. From Figure 6.6, it shows C2 performing slightly worse compared to C1 even though C2 is air entrained. This is because all the control mixes contain GGBS additive which is shown to sometimes perform worse compared to its non-air entrained counterpart. Even with GGBS replacing a certain percentage of CEM I in the concrete, the compressive strength reaches the target strength if not more. As expected, the higher strength concrete performs better in comparison to the other two control mixes.

Oddly, when comparing the results of the concretes in LWA1-3, LWA1 performs worst out of the three despite the concrete being CEM I whereas LWA3 which not only has 55% GGBS replacement but also has 4% chloride salt added to the mix performs significantly better in freeze-thaw and only marginally better than LWA2. This can be related to several variables in the concretes such as the cement type as CEM III/A concretes are known to perform better in freeze-thaw (Bijen, 1996) or the introduction of salt into the concrete would reduce material scaling. Whilst the addition of sodium chloride salt has shown to provide protection for the concrete, it does not mean that it can be used on a concrete element for the simple fact that all concrete elements used in construction use reinforced steel and the sodium chloride salt would corrode the steel.

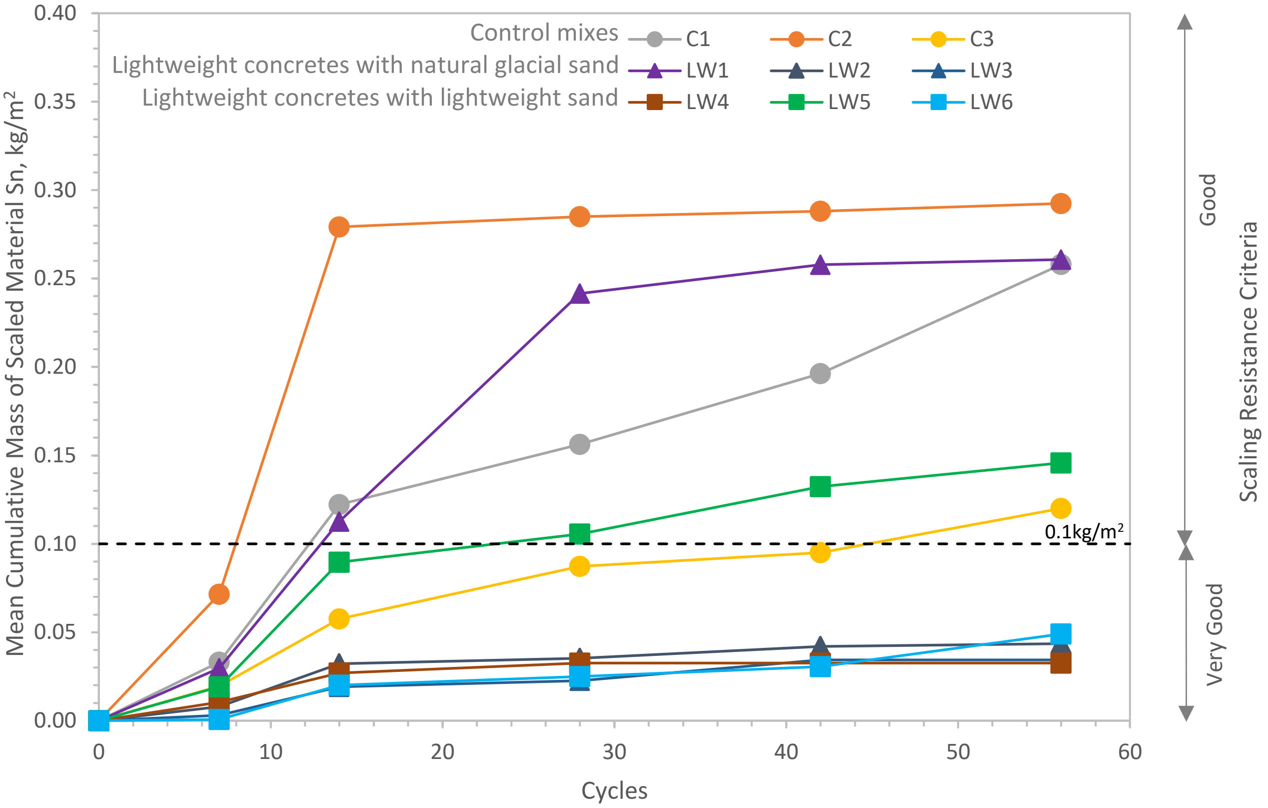


Figure 6.5 Freeze-thaw scaling results for lightweight aggregate concretes

Table 6.5 Scaling criteria results for lightweight aggregate concretes with approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m^2	Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2	Sn_{56}/ Sn_{28}	Rate of Deterioration	Scaling Criteria
	Designated Strength, MPa	w/c	Air Content, %					
C1	C28/35	0.57	0.8	0.26	na	1.63	0.0973ln(x) – 0.1521	Good
C2	C28/35 with air	0.48	5.3	0.29	na	1.00	0.093ln(x) – 0.0483	Good
C3	RC40/50	0.45	1.5	0.12	na	1.33	0.0452ln(x) – 0.0659	Good
LWA1	LC40/44	0.38	2.9	0.26	na	1.08	0.1202ln(x) – 0.1965	Good
LWA2	LC40/44	0.36	3.9	0.04	na	1.0	0.0159ln(x) – 0.0176	Very Good
LWA3	LC40/44 with Cl	0.38	3.7	0.03	na	1.5	0.0149ln(x) – 0.0238	Very Good
LWA4	LC40/44	0.38	4.9	0.03	na	1.0	0.0102ln(x) – 0.0049	Very Good
LWA5	LC/40/44	0.36	5.5	0.15	na	1.36	0.057ln(x) – 0.0802	Good
LWA6*	LC40/44 with Cl	0.38	5.0	0.05	na	2.5	0.0196ln(x) – 0.0365	Very Good

Na – not applicable

*achieved a very good rating overall but the Sn_{56}/Sn_{28} value is over 2kg/m^2 meaning that it has an unacceptable rating

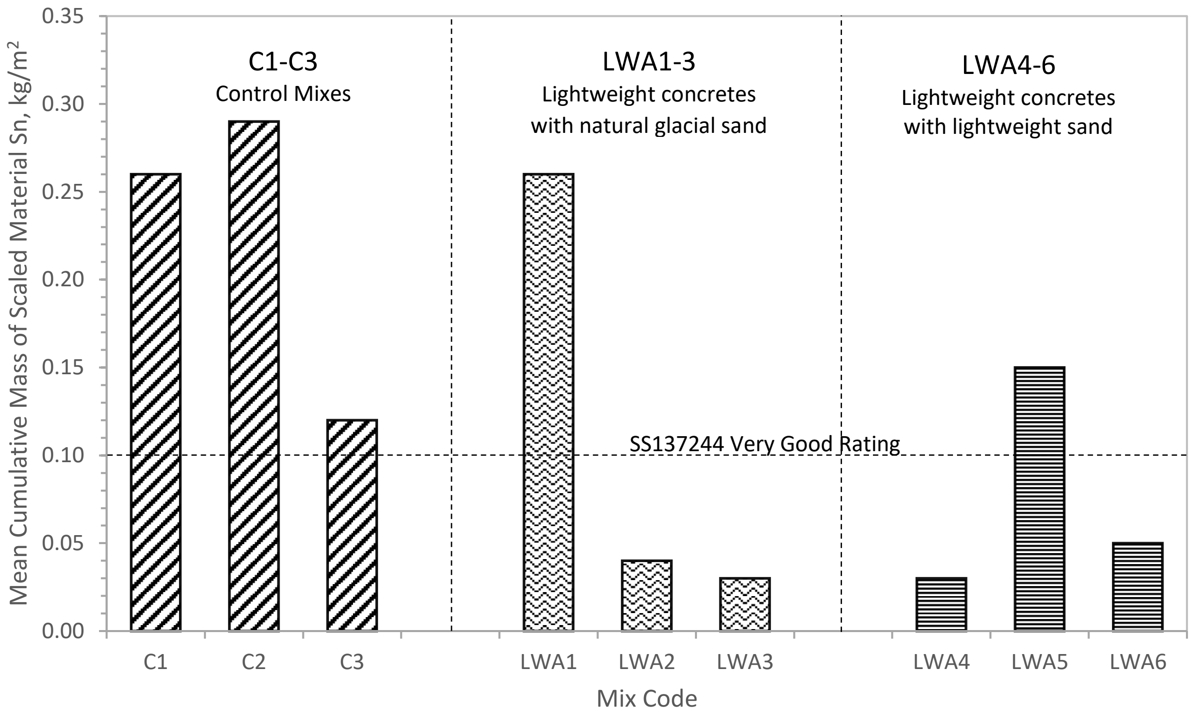


Figure 6.6 Comparison of the lightweight concretes after 56 cycles of freeze-thaw testing

LWA4-6 shows different result in comparison to C1-C3 and LWA1-3 with one parameter change being the replacement of the natural glacial sand with fine lightweight aggregate. Compared to LWA1, LWA4 performs significantly better than LWA1 with just the change of the fine aggregate which would relate to the fineness of the lightweight particles. Since the lightweight particles are finer than natural sand it allows the particles to fill any small voids in the concrete reducing the amount of entrapped air voids. This would force the water to move into the voids of the lightweight aggregate and cause expansion to occur, therefore, damage the aggregate rather than the concrete, hence the reduction in the mass loss.

Theoretically this would reduce the scaling however the results for LWA2 and LWA5 do not agree with the analysis. As the results show the scaling for LWA2 is minimal giving a very good scaling rating so in theory the results from LWA5 should be little to no scaling but the data shows differently with LWA5 giving the highest scaling value for LWA4-6. This can be linked to the different fine material in the concrete. LWA5 is a CEM III/A concrete which uses lightweight coarse and fine aggregate and as already discussed, lightweight aggregate is made from fly ash. Thus, using CEM III/A concrete which has 55% replacement of GGBS can be construed as a tertiary concrete because of the fine lightweight aggregate. If this is the case then not only does the concrete have reduced strength from GGBS replacement and using lightweight aggregate, but the fine aggregate would act as a cement compound further reducing the strength, hence, reduce the performance of the concrete during freeze-thaw attack.

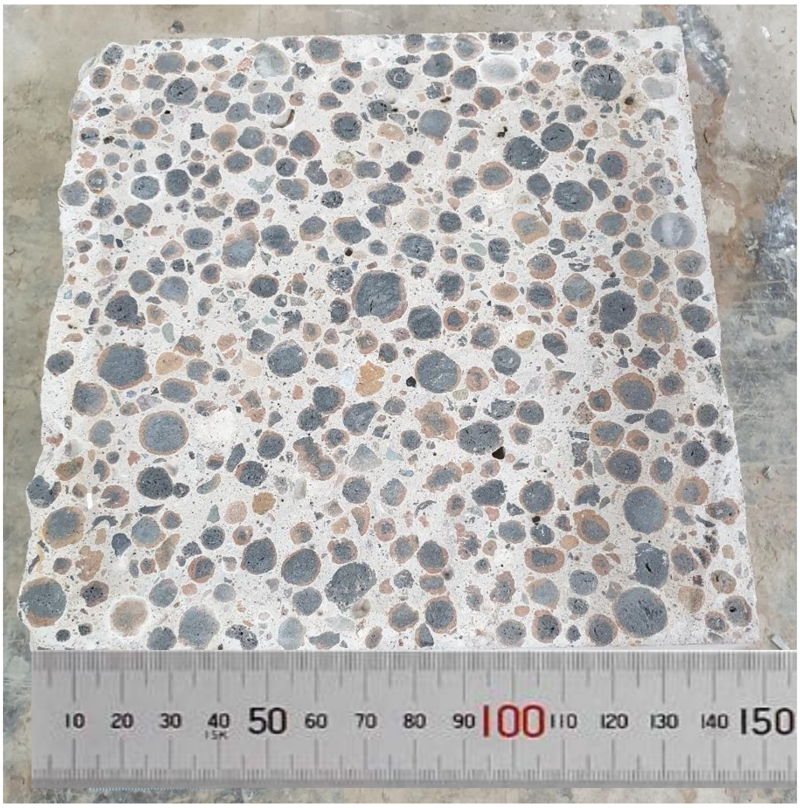
The introduction of sodium chloride salt into the concrete is not common practice as it does increase the corrosion rate of the steel reinforcement. LWA3 and LWA6 performed better than majority of the other concretes both achieving a *Very Good* scaling rating. This reduction in the scaling of the concrete relates to the lightweight aggregate absorbing the saline solution during the freezing and thawing cycles causing the salt particles to remain in the aggregate once the water has dried out. After each application of the saline solution and the multiple cycles the samples are subjected to the salt concentration builds in the aggregate pores and whilst it prevents the concrete from scaling, the aggregate begins to scale instead due to the crystallisation pressure from the build-up of the salt crystals in the pores. Figure 6.7 shows LWA3 and LWA6 after 56 cycles showing the scaling of the aggregate rather than the cement paste.

This trend in the scaling of the concretes supports the previous statement that concrete performs better in freeze-thaw when it has been air entrained rather than the concrete's design strength increased. Described in Table A9 from BS8500, the concretes are required to be high strength with no air entrainment or lower strength with air entrainment but concrete containing lightweight aggregate (LC40/44) sits in between the two opposite ends of the spectrum. Whilst lightweight aggregate concrete design shows to have a slightly higher compressive strength compared to the air entrained concrete and lower than non-air entrained, the design is purposely placed between the two because the resisting properties would then have the best of both with a higher air content without the use of air entrainer but not needing additional cement to counteract the loss in strength due to the addition of air entrainer. Moreover, the concrete would then be lighter compared to normal concrete allowing structures to have reduced weight and still be capable to be as strong as normal aggregate concrete.

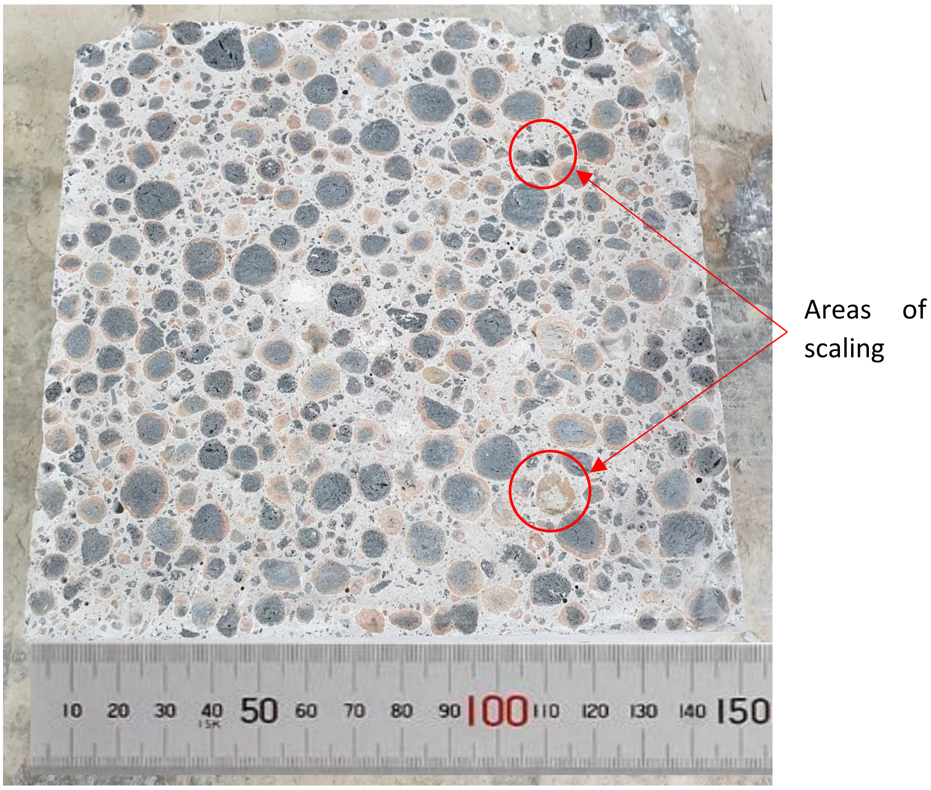
6.3.1 Effects of Lightweight Aggregate's Air Void Characteristics on the Freeze-Thaw Resistance of Concrete

In the previous section, the freeze-thaw resistance of the lightweight aggregate was analysed and found that the concrete containing the aggregate out-performed its higher strength and air entrained counterparts. This section will look at the influence the air void parameters had on the freeze-thaw resistance and why this material was able to withstand freeze-thaw attack.

According to the results in the earlier section the lightweight aggregate had the capability to achieve a *Very Good* scaling rating in accordance with the Swedish standard SS 137244 which was what European CEN/TS 12390-9 test method is based upon. This means that with lightweight aggregate, these concretes would be the preferred option for XF conditions. Though this is true, there is little understanding on why the concretes perform better than normal aggregate concretes. Figure 6.8 shows the comparison between the air content in the hardened state and the scaling.



a)



b)

Figure 6.7 Photos of (a) LWA3 with no visible surface scaling and (b) LWA6 showing some scaled areas after freeze-thaw testing after 56 cycles (scale in mm)

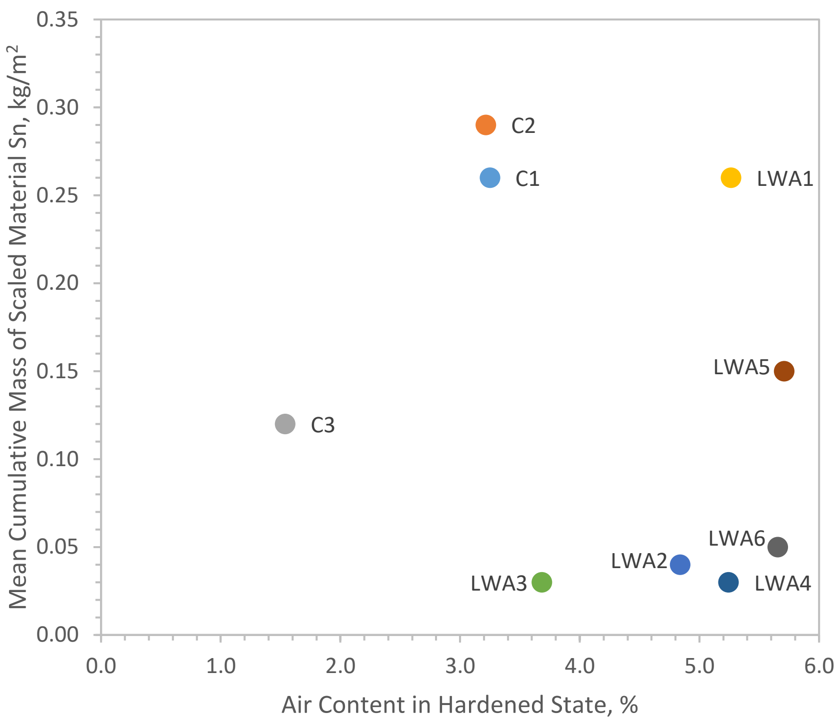


Figure 6.8 Comparison between the air content in the hardened state and the scaling of the concretes

Ordinarily, when a concrete has higher air content, the amount of scaling is reduced showing a direct correlation between the results, although, despite having air entrainment the concrete is still subjected to cracking imposed by the solution in the voids. As depicted in the figure, the values illustrate that even with the higher air content, there is still more scaling as shown by LWA1. This could be the result of the aggregate scaling rather than the cement paste (as described earlier) meaning that if the aggregate is the only thing that is scaling then technically the aggregate or *air entrainment* is doing what it was designed to do, to reduce scaling of the concrete and prevent cracking internally and to the surface. The consequence, however, would be that continual freeze-thaw attack on the aggregates could lead to complete degradation of the aggregates resulting in an aggregate sized void in the concrete. If the concrete is under heavy compression there is a possibility that these voids can create weak spots causing cracks, spalling or even possible collapse.

Understanding how the lightweight aggregate affects the air void characteristics provides detailed analysis on how the concrete, as a whole, will react in freeze-thaw conditions. As with air entrained concretes, the characteristics are analysed to identify specific values which each parameter is required to be to be able to withstand freeze-thaw cycles. Regarding the lightweight aggregate, these are essentially air entrained aggregates being added to the concrete mix. So rather than having normal aggregate combined with air entrainer in the mixing process, lightweight aggregate is a mixture of the bulk material added to increase the volume with the combined benefits of an air entrainer without having to adjust the cement content for the addition of air entrainer.

Figure 6.9 shows each of the air void characteristics to the total loss of scaled material. As with the results seen in Chapter 5, there were discrepancies regarding the expected values and the values shown. Specific surface is determined by calculating the surface area of the air voids and dividing them by their volume. This should indicate that the non-air entrained concrete (C3 – RC40/50 XF) should have the lowest specific surface when compared to the rest of the concrete where they have a higher void count due to the air entrainment or the voids in the aggregate. However, this was not the case as shown in Figure 6.9a, C3 had a similar value to LWA4 and was better than C2 which was an air entrained concrete. This result, coupled with the results seen in Chapter 5, clearly show that when comparing samples using the specific surface against scaled material loss there is little correlation in the data.

The Spacing Factor characteristic is a very unreliable parameter to use as the results produced provide no correlation to each other and in some cases no sense at all. Figure 6.9b shows the results for the spacing factor plotted against the total scaled material loss. As shown, the results do not provide a correlation, thus, a conclusion to be based off. Ordinarily, an air entrained concrete (or lightweight aggregate concrete) would have a smaller spacing factor than a concrete which does not have air entrainment. However, the figure shows that C1 (a non-air entrained concrete) has a better spacing factor value than C2 (an air entrained concrete) which is not correct as these results should be the other way around. C3 should have a larger spacing factor value compared to the rest as it does not contain air entrainment (which it does) but it remains below the 250μm threshold meaning that according to Powers (1945) original hypothesis, any spacing factor value lower than 250μm should have the capability to withstand freeze-thaw attack, however, C3 is not air entrained so technically it would have to depend solely on its compressive strength.

When Powers (1945) derived this hypothesis, it was for air entrained concretes to ensure they have a spacing factor lower than 250μm, anything above this value would be classed as non-air entrained. Overall, if further calculation were to consider the spacing factor a base value for analysis then the parameter would have to be modified to consider new admixtures with secondary benefits.

Apart from one outlier, the void frequency would be the better option for comparing the results. Figure 6.9c shows the void frequency for the concretes against the total scaled material loss. If the outlier (C1) was removed from the figure, there is a trend seen where a lower void frequency measure for the non-air entrained concrete and higher for air entrained. The void frequency is the measure of the voids intercepted by a traverse line divided by the length of that line.

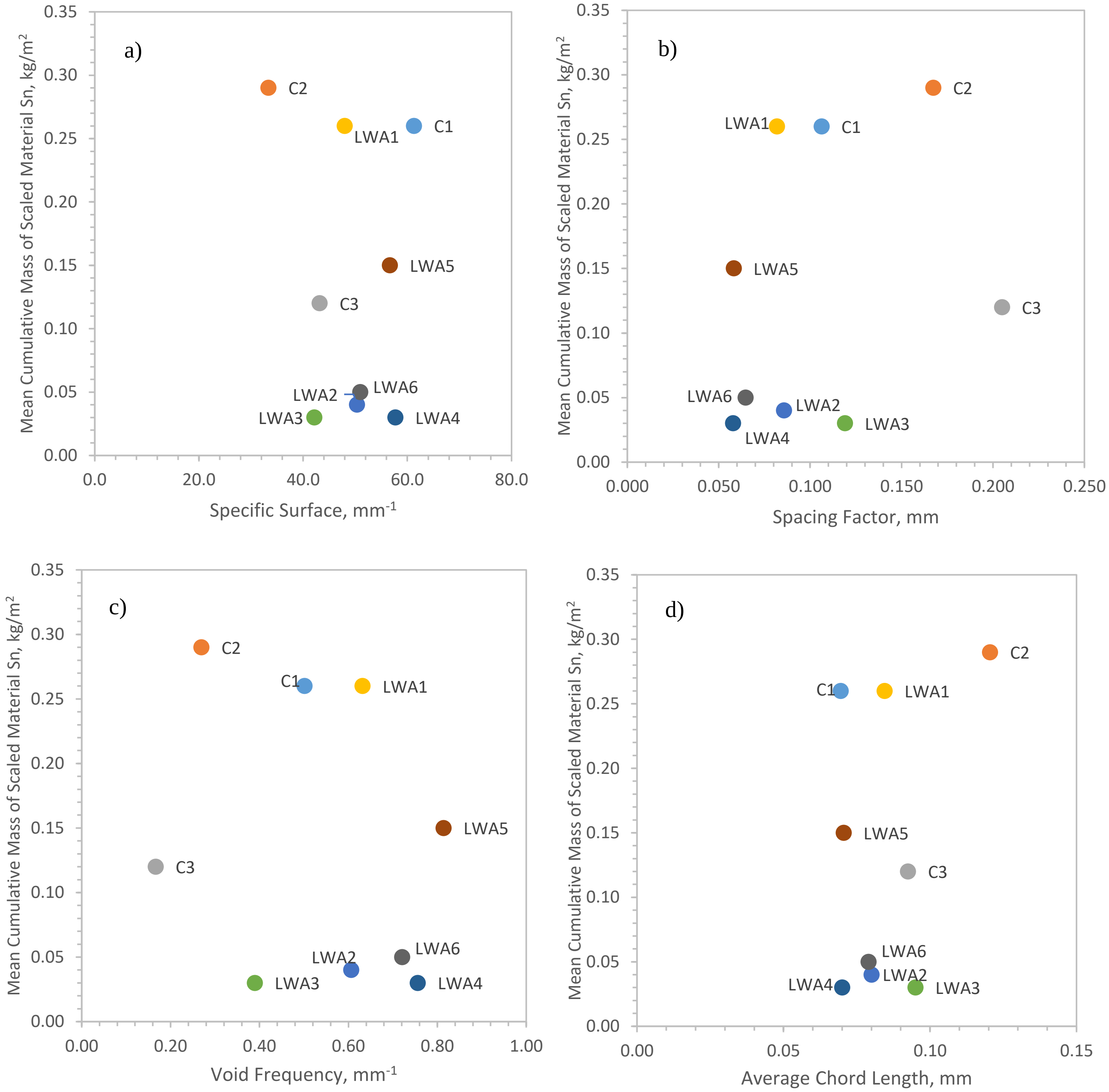


Figure 6.9 Comparison between freeze-thaw scaling and (a) specific surface; (b) spacing factor; (c) void frequency; and (d) average chord length for concretes containing lightweight aggregate

Figure 6.9d shows the average chord length for each of the concretes. The average chord length is an average of all the void sizes to produce the single average length for the sample. This parameter is very inaccurate because if there is a high count of small voids in a non-air entrained sample (as counted for C3) then it inaccurately produce a result which would state that the average chord length for that sample was similar to an air entrained concrete, therefore, it would have the capability to withstand freeze-thaw attack. Moreover, from the figure, it was observed that the data determined that C1 (non-air entrained CEM III/A 35MPa concrete) would be better to resist freezing and thawing than a higher strength 50MPa concrete or an air entrained 40MPa concrete.

Comparing all the parameters overall for an air entrained concrete to a concrete containing lightweight aggregate concrete is shown in Table 6.6. As shown, the results for each characteristic are similar to each other meaning that there is a possibility that if air entrainment cannot be used in a concrete mix then rather than using freeze-thaw resisting aggregates, lightweight aggregates should be used instead.

Table 6.6 Comparison between the air void characteristics for an air entrained CEM III/A 40MPa concrete containing normal aggregates to a non-air entrained CEM III/A 40MPa concrete containing lightweight aggregates

Air Void Characteristic	CEM III/A Air Entrained[1]	CEM III/A Non-Air Entrained[2]
Air Content, %	5.1	4.8
Spacing Factor, mm	0.067	0.086
Specific Surface, mm^{-1}	68.59	50.36
Void Frequency, mm^{-1}	0.876	0.607
Average Chord Length, mm	0.059	0.080
Microair Content, %	3.83	3.66

1) CEM III/A Air entrained refers to the concrete containing freeze-thaw resisting aggregates
2) CEM III/A Non-air entrained refers to the concrete containing lightweight aggregates

6.3.2 Lightweight Aggregate Resistance to Freeze-Thaw Conditions (Freeze-Thaw Test on Aggregate – BS EN 1367-1)

In regard to freeze-thaw, the aggregates are required to be XF4 compliant meaning that when subjected to the magnesium sulphate (MS) test they must have a total mass loss less than 18% of the total mass to be suitable for XF4 conditions. The granite tested had an MS value of 1 allowing the material to be used in concrete subjected to freeze-thaw condition whilst gravel has a value of 23 meaning that it is only suitable up to and including XF3 conditions. Lightweight sits at the opposite end of the spectrum whereby the material provides *Very Good* rating in accordance with SS 137244, however, when the aggregate was tested using the MS test the aggregate disintegrated giving a final result of 38 which details that the material is unsuitable for any XF conditions.

Understandably, the aggregates are tested harshly so that they do not fail during freezing and thawing cycles. As with the freeze-thaw test method the concrete samples are tested harshly to temperatures which are not seen in the UK. Because of this the results of the MS test were compared to the results of the freeze-thaw test for aggregates BS EN 1367-1 which puts the aggregates through the similar freeze-thaw conditions as concretes.

BS EN 1367-1 is the aggregate freeze-thaw equivalent of the BS EN12390-9 test method for concrete. The coarse aggregate was placed into metal cans with water and tested to similar temperature profile to freeze-thaw test method with the aggregates saturated in water for the duration of the test. From the test, the results show the lightweight aggregate performs just as well as granite. This shows that the two test methods which were intended to test the aggregate to achieve the same result in fact give completely different values.

This study is to look at how the aggregate influences freeze-thaw resistance in a concrete. One aspect which was investigated was how the aggregate prevented freeze-thaw deterioration by absorbing the chlorides from the saline solution. As shown lightweight aggregate can reduce the effects of freeze-thaw damage to the cement paste by absorbing the water into the pores and allowing the ice to expand within the aggregate without affecting the cement paste. This was tested with the introduction of chlorides into the concrete which showed a reduction in the amount of scaled material.

During the study it was discussed that the lightweight aggregates would absorb the chlorides during each cycle. In order to replicate this, a mass of lightweight aggregate was subjected to wetting and drying in saline solution for 48 hours (24 hours wetting and 24 hours drying). This process was repeated 10 times to ensure the aggregate had salt crystals built up in the pores. Once the wetting and drying process was complete the aggregate was tested using the freeze-thaw test method for aggregates comparing lightweight and lightweight with chlorides to understand if the chloride saturation influenced the freeze-thaw resistance (Freeze-thaw test on aggregates – Chapter 3). Granite was also tested as a reference as it is classed a freeze-thaw resisting aggregate.

From the test, the results show that the both the lightweight aggregates shown to have a very high resistance to freeze-thaw meaning that according to BS EN 1367-1, they satisfy the requirement to be used as freeze-thaw resisting aggregates. However, this contradicts the results from the MS test whereby the lightweight did not manage to be classified on the MS scale (Table 3.3). The MS test is the recognised test method when determining which aggregates are suitable for freeze-thaw. Although, as with the CEN 12390-9 test method for concrete, it was pointed out that the MS test is very harsh because of the heavily saturated solution which then infiltrates the voids then expands inside the voids causing the aggregate to burst under the pressure exerted on the pore walls. Moreover, due to the size of the voids in the lightweight aggregate, there is very little room for expansion in comparison to gravel which is also a porous material.

Since lightweight material is manufactured from fly ash, the size of the lightweight does not get any bigger than 14mm it then becomes difficult for the material to withstand the internal pressures from the

MS expanding. Whereas gravel, that has sizes up to 20mm, had much larger pores more visible to the naked eye. This means the MS solution has more room to expand within the material, thus a reduction in the material loss.

Overall, because of the viscosity of the MS solution and the size of the material it is very difficult for lightweight aggregate to be classed as a suitable freeze-thaw conditions in accordance with BS EN 1367-2. However, from the freeze-thaw results above for the concrete containing lightweight and in accordance with BS EN 1367-1, lightweight has the capability to withstand freeze-thaw deterioration despite the results from the MS test.

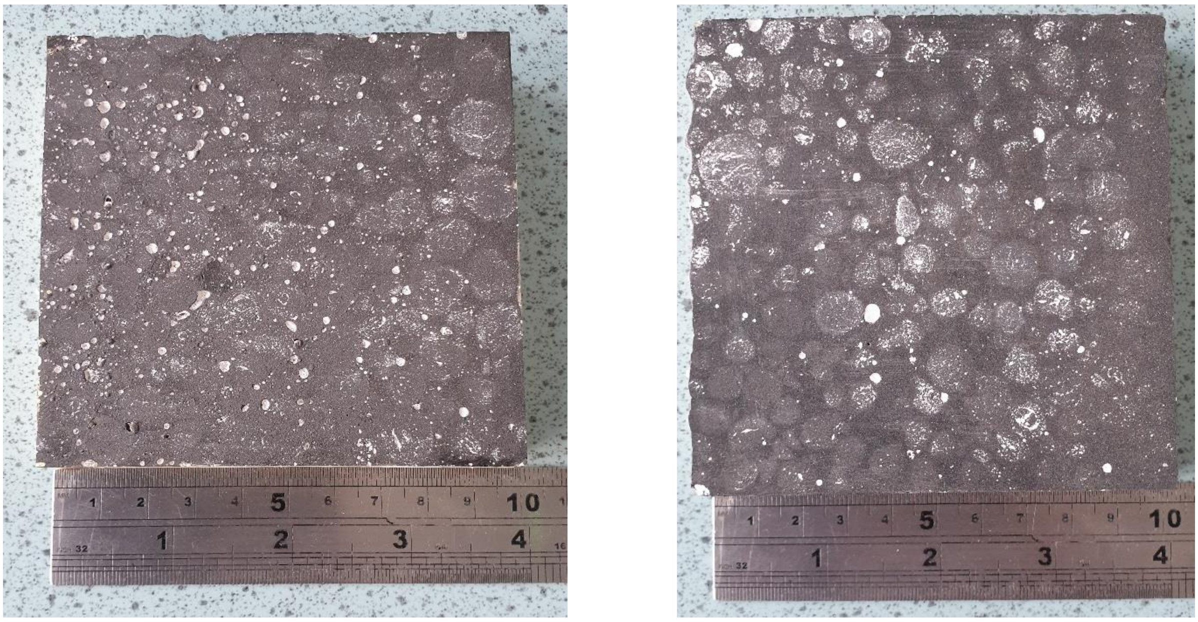
6.4 Influence of Lightweight Aggregate on Microstructural Properties of the Air Void System

As previously discussed, lightweight aggregate influences the air void characteristics due to the high quantity of voids within the aggregate and because there was a high volume of aggregate, the number of voids counted significantly increases. The air void parameters were analysed in Section 6.3.1, but there was not any differentiation as to how the high number of smaller voids influences the microstructure of the concrete. LWA concrete slices were put through the air void analyser which determined the air void characteristics but also included entrapped air voids as there was not air entrainment added to the concrete.

Ideally, the analysis should be done on the aggregate only that way the air void properties of the cement paste can be ignored. But because the material is small cutting is difficult, so analysis is conducted on a 20mm slice as done previously but rather than using a cement paste the aggregate was cast into resin which removed the voids from the resin *paste* allowing just the voids within the aggregate to be counted only. Figure 6.10 shows the cube cast in resin and the slice used for air void analysis.

Replicating the quantity of aggregates in a 100mm specimen was difficult as there were several issues encountered trying to replicate the number of aggregates in the concrete. The main issue was the density of the *paste* as the resin was not as viscous as typical cement paste meaning that the aggregate sank to the bottom of the moulds leaving about a third of the specimen empty of aggregate. Filling the mould of aggregate was the best option for an even distribution and to identify whether the densely packed material would influence the void count and total air content.

This analysis produced air void results defining the air void characteristics for the aggregates alone. Figure 6.11 shows the comparison between the concrete and resin total air voids counted and Table 6.7 shows the results for the resin air void analysis compared against LWA1 and LWA2 for comparison between the cement type and between how the cement paste and resin to determine how much the lightweight aggregate influences the air void results.



(a) *(b)*

Figure 6.10 Lightweight aggregate cast into (a) resin and, (b) concrete and a 20mm thick slice taken from each cube and used to determine air void characteristics of the aggregate (scale in mm)

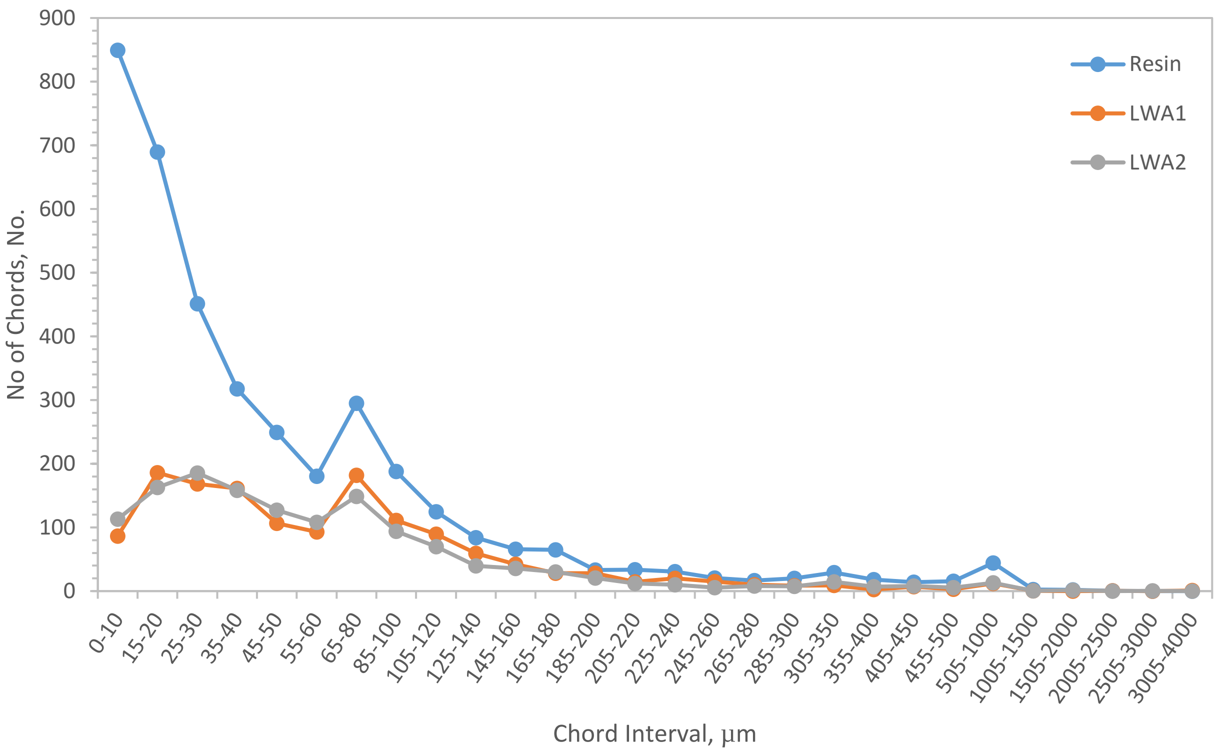


Figure 6.11 Comparison between the total number of voids counted for resin containing lightweight aggregate (Resin), CEM I concrete containing lightweight aggregate (LWA1) and CEM III/A concrete containing lightweight aggregate (LWA2)

Table 6.7 Comparison between the air void characteristics between materials used to determine how the voids in the lightweight aggregate compare to the cement type

Parameter	Resin	LWA1 (CEM I)	LWA2 (CEM III/A)
Air content of hardened material, %	11.0	5.3	4.8
Spacing Factor, mm	0.051	0.082	0.086
Specific Surface, mm^{-1}	61.37	47.97	50.36
Void Frequency, mm^{-1}	1.680	0.632	0.607
Average Chord Length, mm	0.066	0.085	0.080
Microair Content, %	6.8	4.1	3.1

From Figure 6.11, the number of voids counted in the resin is observed to be more than eight times the amount counted in the two concretes showing the effect of adding more aggregate to the resin. Despite the large difference in the voids counted in the 0-30μm range, the trend across all three samples is the same showing a sudden increase in the 65-80μm range and a slight increase in the 505-1000μm. This is also reflected on the air void characteristics shown in Table 6.7. The increase in the amount of lightweight aggregate increases the total air content (as shown) which was expected as more aggregates means more voids.

The number of voids for the resin was observed to be significantly higher due to the quantity of aggregate used in the sample. Since the resin did not have the same density as cement, the aggregate simply sank to the bottom leaving majority of the resin without aggregate. The increase in the quantity of aggregate saw and increase in the air void characteristics, which does not reflect on the total aggregate quantity seen in lightweight aggregate concrete. A typical concrete mix would have a density of 2400kg/m^3 whereas lightweight is in the region of 1800kg/m^3 meaning a quarter of the weight is saved in a structure, if the same cement type is used. Similar principle applies in casting cubes where a weight saving 25% was observed. However, determining the quantity of lightweight aggregate was based upon the same procedure as normal aggregate with the difference being that because lightweight is lighter than standard aggregates, more was required to ascertain the same mass as normal aggregates hence, more material in a certain volume, therefore more voids.

Comparing the two cement type samples, it was observed that there was very little difference in the results which can be a direct reflection on there being no air entrainment in these concretes. Without AEA, the cement type does not influence the air content as this was solely based on the voids within the aggregate and the inclusion of entrapped air.

6.4.1 Micro-CT Analysis of Lightweight Aggregate Concrete Microstructure

Simply comparing the results of resin and cement paste showed that the lightweight material is having an effect on the air content but explaining the reasons behind this is difficult. Whilst the lightweight has shown to provide the air void parameters needed to protect against freeze-thaw attack the same way air entrainment does and putting the aggregate through the harsh freeze-thaw regime, there is still the issue of understanding the reasons why? Why is this material surviving freeze-thaw conditions? Why is a material which is very porous and has a high-water absorption rate still manage to withstand freeze-thaw conditions yet has very minimal surface scaling?

Using the observations seen in the air void analysis it was identified that the total voids counted, and the total air contents of air entrained and lightweight aggregate concretes were approximately equal, defining that lightweight aggregate has similar air entraining properties as air entrained concrete. The values for the air content were based upon the total number of air voids counted using the air void analyser, though as previously stated entrapped air was to be avoided as it creates inaccuracies in the results stating there were more voids in the concrete than there actually were. Whereas using the micro-CT scanner a 3D picture can be created and the picture can be analysed to give a preliminary porosity and air content. Initially, an individual aggregate was measured using the CT software to determine a sample range of voids within the sample which can be used to determine the air void content. Figure 6.12 (a) shows a 3D image of a lightweight aggregate and (b) shows a slice through the aggregate to illustrate the dispersion of voids throughout.

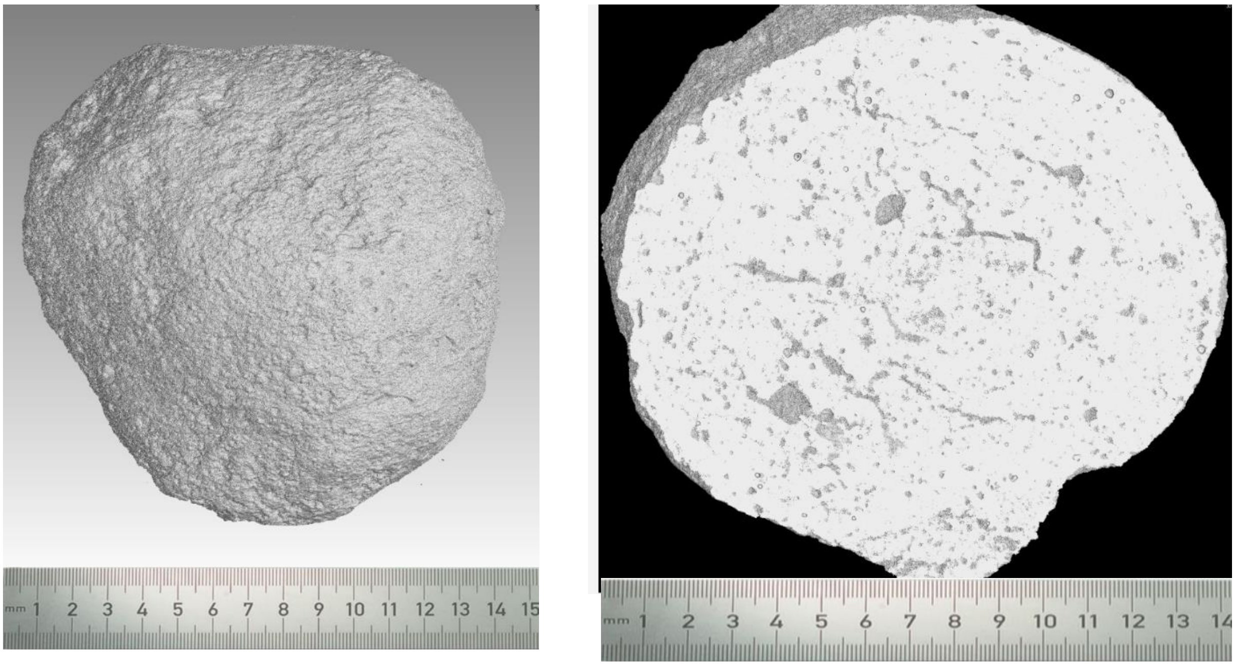
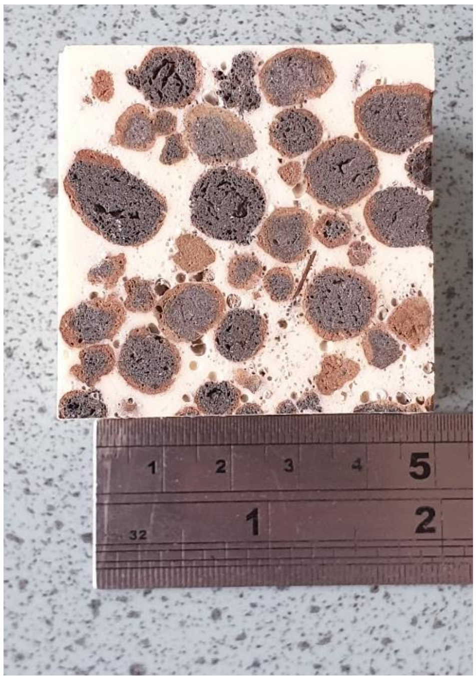


Figure 6.12 (a) 3D image of a an individual lightweight aggregate sample scanned using the micro-CT scanner and (b) a cross sectional slice through the aggregate exposing the voids within (grey/darker shadows)

Given that the aggregate has shown to have air entraining qualities, a small sample was added to resin to identify whether the air voids within the aggregates mimic the air void distribution in an air entrained concrete sample. Figure 6.13 shows two 50mm cubes which were analysed using the micro-CT, one being a CEM III/A air entrained mortar and the other a lightweight aggregate infused resin. Another non-air entrained mortar was also put through the micro-CT for comparison. Once these cubes were analysed by the micro-CT, a series of 2D and 3D images are produced whereby sizes and shapes of the pores could be analysed to a degree.

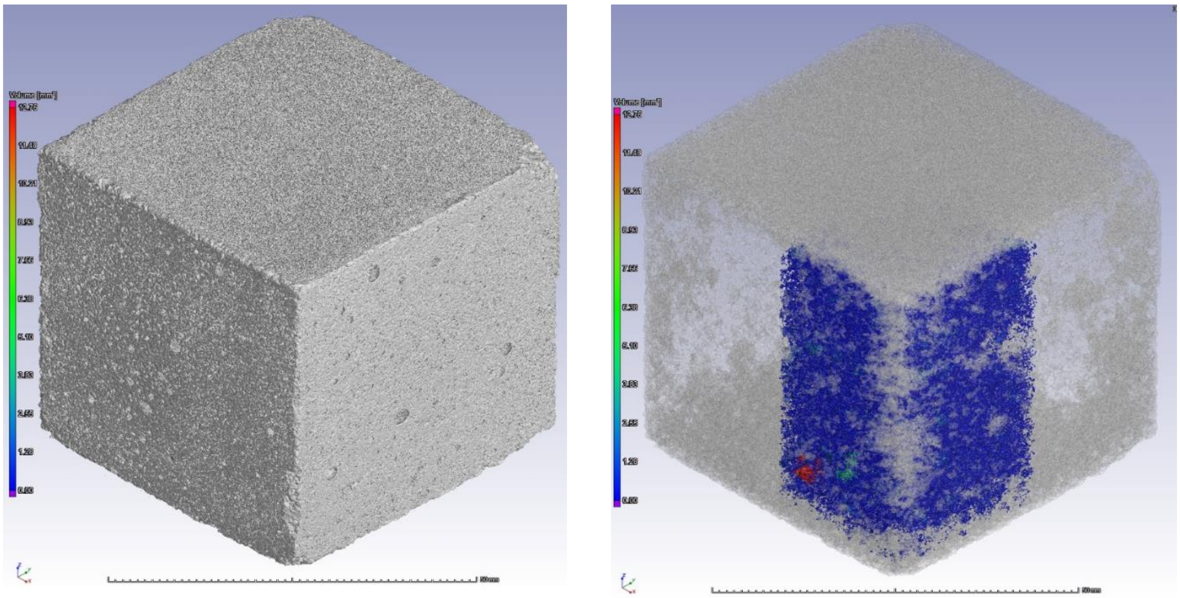
Figure 6.14 shows the computer image of the mortar cube once the micro-CT has analysed the specimen. Due to the high of calculations undertaken to analysis the specimens, only a small section was analysed with detail (Figure 6.14 b). Similarly, concrete samples containing lightweight aggregate were analysed in Figure 6.15 and Figure 6.16.

a)



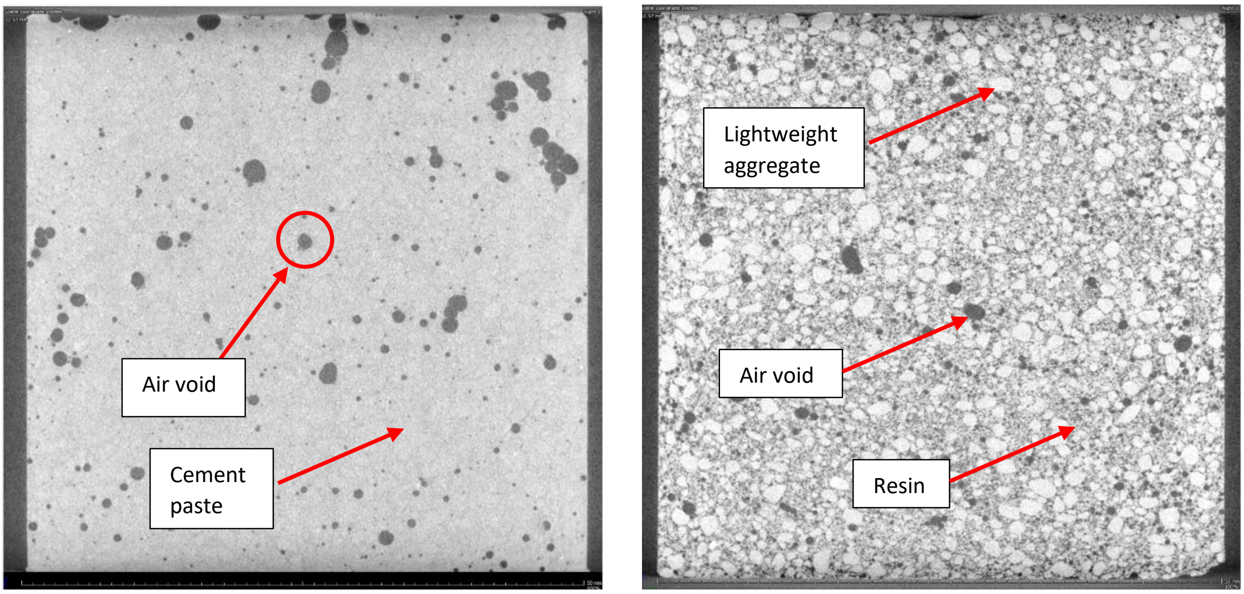
b)

Figure 6.13 50 mm mortar cubes cast for CT scanning a) CEM III/A air entrained and, b) resin cube (scale is in mm)



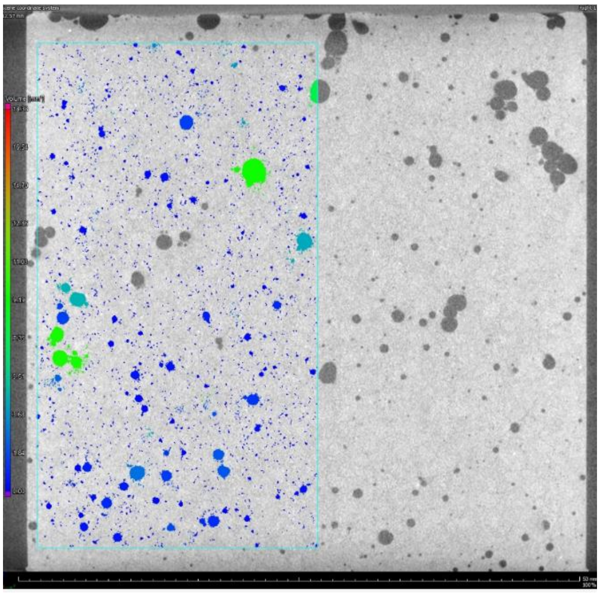
a) b)

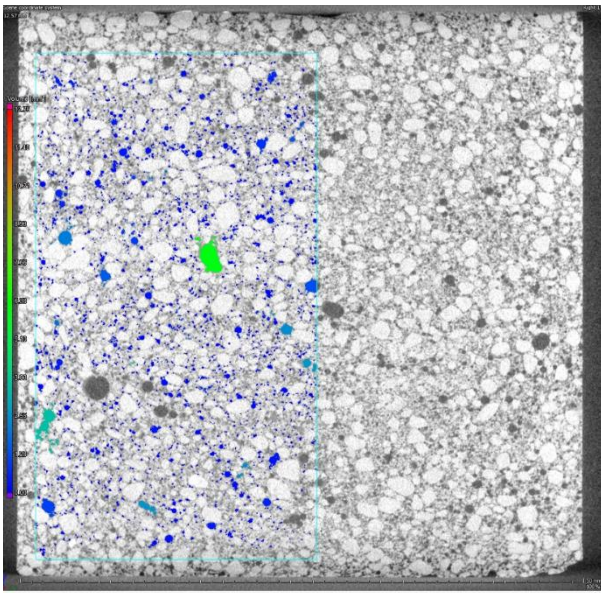
Figure 6.14 a) 3D semi-transparent image of a 50 mm cube and, b) region of the cube analysed for porosity by the micro CT scanner



a) b)

Figure 6.15 Micro-CT image of a 50mm a) CEM III/A air entrained mortar cube and, b) resin cube with lightweight aggregate showing the distribution of voids through a slice of the sample





a) *b)*

Figure 6.16 3D semi-transparent image of a 50mm CEM III/A air entrained a) mortar cube surface and b) virtual cross sectional view of 50 mm cube produced from the CT scanner showing the region analysed for porosity

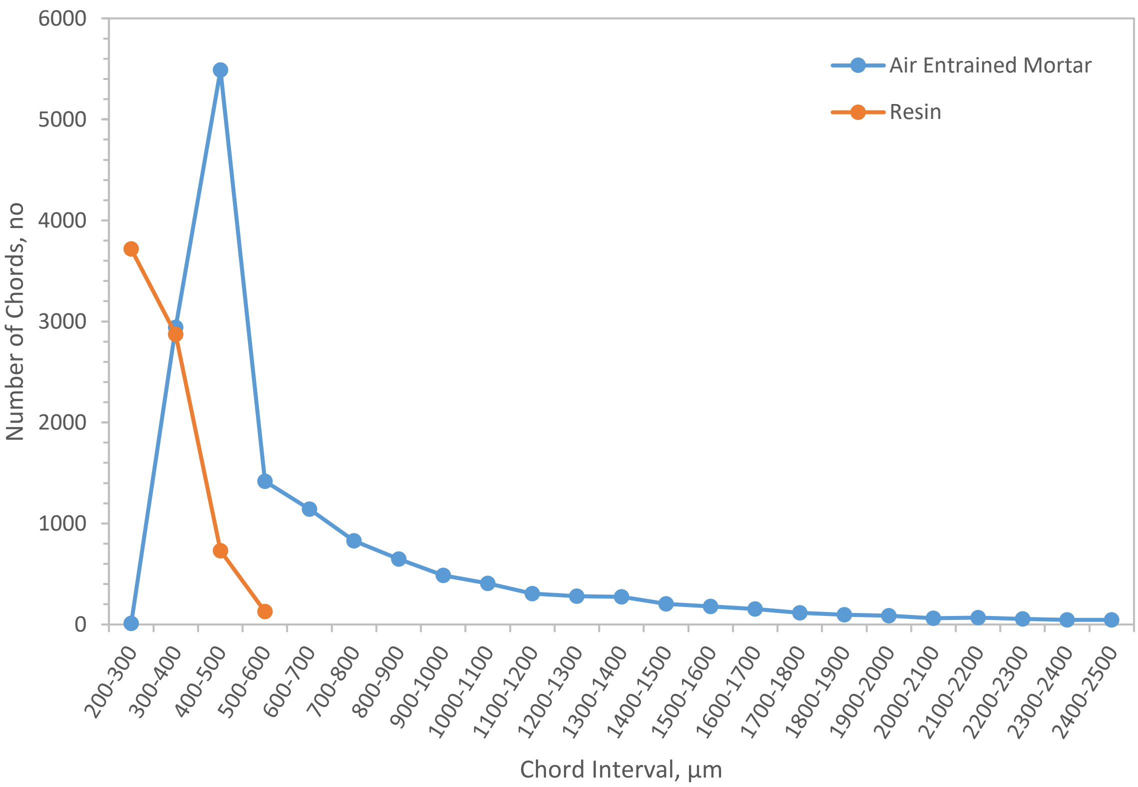


Figure 6.17 Comparison of the number of voids counted using the µCT scanner between the GGBS air entrained mortar and the lightweight aggregate resin

From the analysis using the CT scanner, it was identified that there was a higher void count for the air entrained mortar with most of the void sizes ranging up to 1500µm for the most part. The largest quantity was found to be with 400-500µm range following the data analysed earlier stating that effective air entrainment was below 500µm. The resin only consisted of voids 600µm or less and at a lower count by comparison, however, the resin only had a small quantity of lightweight aggregate and the mortar did not have coarse aggregate both of which would influence the total void count had both samples been compared in full scale concrete samples.

6.4.2 Analysing Lightweight Aggregate Internal Structure

As the air void and scaling results show lightweight aggregate concrete provides very good protection against freeze-thaw attack. But understanding and explaining the reason(s) behind this is more difficult. A study undertaken by Zhang & Gjorv (1990) tested lightweight aggregate for use in high strength concrete. They reviewed the impact of the high-water absorption of the aggregate looking at the microstructure and the characteristics of the aggregate. They found that the aggregates varied depending on the manufacturing process and the void sizes ranged between 4nm and 1mm. In all the aggregates, it was identified that there were relatively large voids that made the aggregate susceptible to fragmenting.

Looking solely on the aggregate itself, various analysis techniques were used to identify the why this aggregate manages to provide very good protection to the concrete. Using techniques such as absorption/vacuum and MIP pore size, the aggregate properties were calculated to determine how the aggregate provides a safeguard for the concrete.

6.4.2.1 Absorption/Vacuum Analysis

Lightweight aggregate is a very absorbent material as shown with a water absorption value of 14% compared to natural gravel for the local area with a value of 2.6%. This very high absorption shows that lightweight material had to be pre-wetted to reduce the loss of free water in the concrete mix. The aggregate was left to saturate in water for 24 hours before being used in the casting to reduce the volume of water lost to any further absorption.

As with concrete, it is impossible to determine whether the aggregate is fully saturated where the principle behind soaking the material in water beforehand was the best technique there is no way to tell if that had been achieved. To confirm if full saturation had been achieved, a small amount of aggregate was place in a container of water and left for 24 hours to determine the initial absorption value. This was calculated to be 14% as previous and then the aggregate was put back into the container of water and placed into a vacuum-oven and the air removed to force more water into the voids of the aggregate. Extracting the air out of the aggregate creates capillary suction forcing more water in whereby nearly full saturation can be reached.

Two samples were tested, and the average taken to determine how close the absorption of the material was before and after vacuum removal of the air. Both samples were shown to have a high absorption rate with Sample 1 being 12.5% and Sample 2 being 13.9% similar to the water absorption value seen earlier. The difference in the values relates to the characteristics of the aggregate such as the fly ash used in the sintering process, the aggregate size and the pore size distribution through the aggregate matrix. Sample 1 and Sample 2 both achieved similar additional absorption values of 1.4% and 1.5% respectively equating the additional absorption to 10.4% increase.

These results suggest that despite the material being manufactured from fly ash where the properties are known to provide poor freeze-thaw resistance, the aggregate itself provides a means of removing significant amounts of water out of the cement pores reducing deterioration. Moreover, with the aggregate left soaking in water prior to use, not only does it prevent the aggregate from absorbing the free water in the concrete but also has an additional 10% capacity.

6.4.2.2 Mercury Intrusion Porosimetry (MIP)

Mercury Intrusion Porosimetry is a technique utilized to determine the porosity, pore size distribution and pore volume of different materials. The technique uses a pressurized chamber to force mercury into the voids of the material. It starts with the larger voids first before forcing into the smaller voids as the pressure increases. This allows for all the pores within a sample to be fully characterised.

Several small lightweight samples were used to generate a sample measurement of the total pore characteristic with a concrete specimen. Three individual pieces of aggregate were collected and broken up to expose the internal microstructure for the analysis to be done, with various sizes selected and placed into the chamber. Unlike the air void analyser where the number of voids were counted in 2D and totalled up at the end, MIP measures the total number of voids within the sample as the total volume for a particular size of void. Equation 6.1 describes the calculation used to determine the distribution of the voids within the material:

$$Distribution\ Function\ (Fv) = \frac{Pore\ Volume\ Distribution}{Pore\ Diameter} = -\frac{dV}{dlogD} \tag{6.1}$$

The calculation determines the distribution for each of the void diameters using the distribution function (Fv). This translates into the total volume for a particular pore size which would equate to the total number of voids determined using the air void analyser. Figure 6.18 shows the distribution of pore sizes throughout the sample as a function of the distribution.

As the figure shows, the total volume distribution throughout the aggregate peaks at 7µm which correlates to the chord size group, 0-10µm, of voids counted during the air void analysis of the resin containing lightweight aggregate. The issue with the comparison is when using the automated air void analysis, the results only show how many voids are counted within a chord size range rather than measuring the size of each individual void size. This correlation also provides validity in that using automated air void analysis (which is relatively new equipment) does provide similar results to those from other testing techniques such as the air void analyser.

Whilst there is a clear distribution of void sizes throughout the aggregate samples, peaking at 7µm, consistent with data analysed for the air void analysis, it was observed that there is another peak at 0.7µm suggesting a high number of voids of this size. This would correlate with the higher quantity of voids counted in the air void analysis albeit this is measured in a range of 0-10µm, but it may partly answer why there is a spike in the MIP.

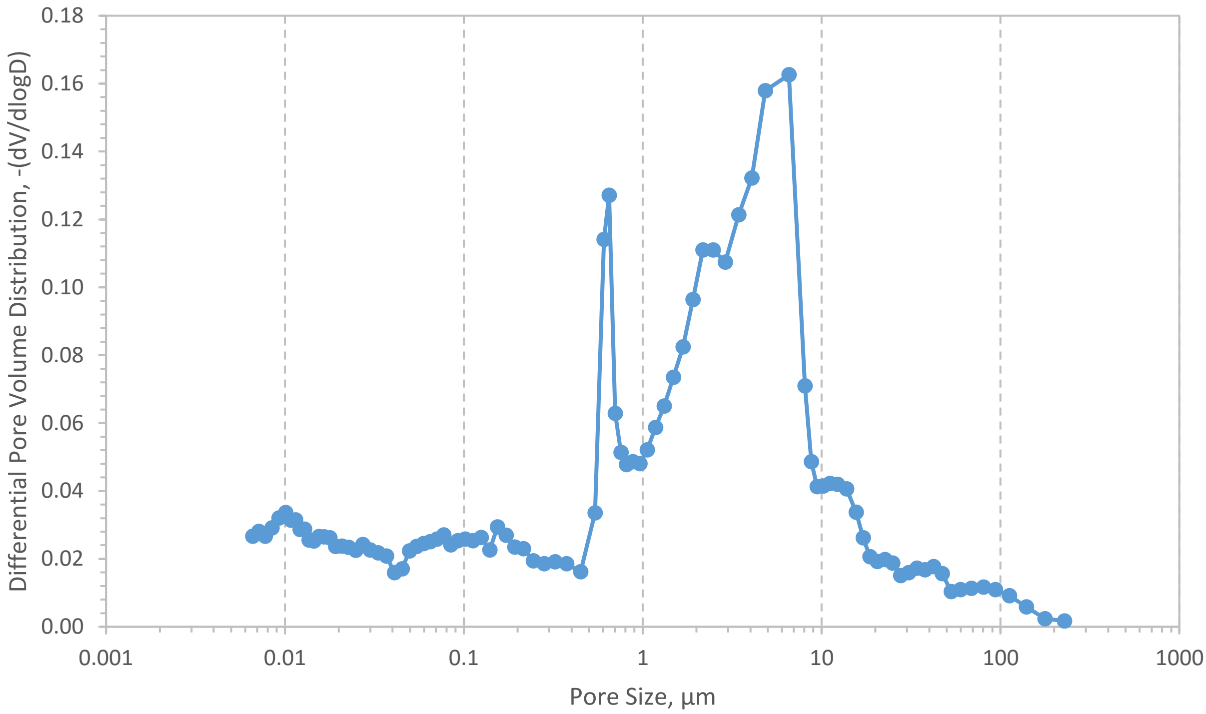


Figure 6.18 MIP results showing pore size distribution inside a lightweight aggregate sample as a function of the distribution

Quantifying the results shown in the various analysis methods above outline comparisons to determine not only the air void analysis such as range of void sizes, spacing factor and air content but also a way to verify if the results produced by the automated analysis are comparable or inaccurate. However, using these methods do not necessarily mean that the data collected is accurate. Whilst MIP does give approximation of the void sizes within a small sample, that is all it is a small sample which may not give the representation of the entire sample. That being said any microstructural analysis can come to the same conclusion as the air void analysis reviews only a slice from a sample rather than the whole sample.

On the other hand, the µCT scanner is able to give detailed analysis of a sample but like MIP, it can only focus on a small area due to the computation power required to carry out the analysis. On the small areas highlighted above, the analysis took several days to complete due to the amount of analysis required. A possible solution to this would be to combine the analysis from the air void analyser and µCT scanner. The sample would be analysed by the µCT scanner to determine the void sizes and quantities within each chord range the data run through the calculations in the air void analyser to provide a more accurate distribution of the results.

6.5 Summary of Chapter 6

The main objective of this chapter was to identify whether lightweight aggregate has similar microstructural characteristics as air entrained concrete and to determine why the lightweight aggregate reduces the total mass loss during scaling. Concrete subjected to freeze-thaw conditions are required to have freeze-thaw resisting aggregates with the inclusion of air entrainment depending on the design strength in accordance with Table A.9 in BS 8500-1. For XF3 and XF4, Table A.9 details three options to choose from to prevent freeze-thaw scaling:

i. A normal strength concrete (say C28/35) with air entrainment;
ii. A concrete with a higher strength such as C40/50 with no air entrainment ,or;
iii. A concrete with slightly higher strength than normal concrete with no air entrainment but instead lightweight aggregate as the coarse material.

During this study these concretes were represented and compared to one another to determine which was more suited to freeze-thaw conditions to provide a reduction in the total mass loss due to scaling. Control mixes were designed and tested following the minimum requirements for non-air/air entrained normal concrete and high strength non-air entrained as depicted in Table A.9 in BS 8500. The other concretes were designed to the minimum requirement for lightweight aggregate concrete changing between CEM I and CEM III/A cements, normal and lightweight fine aggregates and the difference in the scaling with the inclusion of salt into the design mix.

During the study it was considered that the lightweight aggregate provided an additional benefit against freeze-thaw reviewing a study on a local bridge constructed using lightweight aggregate. This derived the following hypothesis:

The addition of salt into the concrete designs was an attempt to understand whether the lightweight concrete had the ability to absorb the salt and prevent further ingress. With a high-water absorption value, the lightweight material would absorb a high quantity of saline solution, which would dry out in the aggregate leaving the salt crystal, and the same process would begin again creating a "salt defence" against ice infiltration.

Overall, it was found that despite having no air entrainment in the concrete, lightweight aggregate concretes (including lightweight sand replacement) provided better resistance to freeze-thaw than the three control mixes. Detailed analysis using different methods such as air void analysis, MIP and micro-CT analysis showed that the lightweight aggregate material has very similar properties as air entrained normal concrete due to the distribution of smaller void sizes (classed as the microair content in accordance with BS EN 480-11). Comparing the samples, the air entrained controlled concrete (C2) achieved an air content of 5.3% in the fresh state whereas the concretes containing lightweight aggregate were averaging 4.5%, the target air content for this study.

Although it should be noted that even though this value was reached there is no guarantee that this result can be achieved constantly. As the results show the values for the air contents for lightweight aggregate concretes is seen to range from 2.9% to 5.5% depending on several factors including the total amount of aggregate used which influences the number of voids analysed, superplasticizer dosage, compaction and entrapped air percentage.

Chapter 7
Modifying the CEN/TS 12390-9 Freeze-Thaw Test

7.1 Introduction

This chapter examines the impact of changing the CEN/TS 12390-9 test parameters to present a more realistic representation of typical extreme climate conditions in the UK and Europe on the freeze-thaw resistance of concrete. The current test method subjects concrete to extreme temperature variations rarely seen in the UK. These temperatures reach -24 to +24°C (maximum and minimum of the temperature envelope) during the test and whilst it is a good method of testing to ensure the concrete can withstand severe temperature changes, the test has been considered to be too harsh (Harrison et al., 2001) as recent data (Chapter 2) shows the temperatures do not extend that low.

Whilst the standard test examines the performance of one specific concrete surface within the sample, the test does not consider the material lost on the covered sides and base as tested samples during this research project have shown. This phenomenon is unique in the sense that the test is designed to focus on the exposed (saturated) test surface to determine scaling loss during freezing and thawing temperatures and this loss in material around the sides should not be occurring as it is only the test surface which is saturated. This could relate back to Klieger (1990) where it was stipulated that the outer layer of a concrete sample was of the poorest quality which would degrade quickly compared to the middle of the sample, coinciding with what was seen with the outer layers of non-test surfaces spalling with the test surface. During the test the surface is covered in a 3% NaCl solution to encourage scaling and the expansion of ice during freezing causes the concrete to spall. Even though there is not any material loss on the test surface the sides and base has shown to have significant scaling, so analysis was conducted to determine the impact of the additional scaling from the sample's sides and base after testing was completed.

The centre (middle) section of the concrete sample was tested for freeze-thaw in accordance with CEN/TS 12390-9, where the concrete is considered to be the most uniform and the centre of the concrete is deemed to be less variable (Klieger, 1990), but it is not the centre of the concrete which is exposed to environmental elements but instead the cast surface. CEM I, CEM II/B-V, CEM III/A and CEM II/A-L were cast and the cast surfaces were tested to determine how the concrete would perform compared to the standard testing surface. These concretes were chosen as they represent the more common concretes used globally and are well defined in BS EN 206 and BS 8500, with the exception of CEM II/A-L which was chosen because it has recently been added to BS EN 197-1 as a cement replacement rather than a filler.

The CEN/TS 12390-9 freeze-thaw test requires a 3% NaCl solution on top of the test surface to induce scaling. The test describes either using deionised water or a saline solution as an alternative, however, this project used NaCl solution to look at the effects of the NaCl concentration on the concrete which would closely represent real conditions in the winter. However, from Chapter 2, it was understood that the concentration of NaCl on a concrete element in the field is not fixed (it is fixed at 3% NaCl in the test) but instead increases and decreases with each additional application when de-icing salts are applied to the surface (at a rate of 20g/m^2 as detailed by Dundee City Council and Transport Scotland) and the constant precipitation through the winter months. This was considered and a series of tests were conducted looking at the effects of increasing NaCl concentration on the concrete surface.

Moreover, the test method does not consider other external durability factors such as the influence of surface carbonation or the presence of chloride ingress on the freeze-thaw performance of the concrete. Freeze-thaw does cause some damage to the concrete however it is more plausible that freeze-thaw degrades concrete with another external durability factor. A combination of freeze-thaw and carbonation were tested on both air and non-air entrained concretes of different cement types with the same design strength in a bid to determine the effects of the two durability factors on the concrete. These carbonated samples were tested against non-carbonated versions to determine how carbonation affects the concrete during freeze-thaw attack.

7.2 Changing the Temperature Profile to Closer Represent UK Climate

One of the key parameters is the temperature profile the test cycles through every 24 hours. The CEN 12390-9 standard dictates the temperature can cycle between +20°C (±4°C) to -18°C (±4°C) and the freeze-thaw testing chamber was pre-set to +23°C and -18°C which falls with the temperature ranges for the CEN test. In order to determine a suitable temperature profile, the CEN test temperature profile was modified to look at how the differences in the temperature affects the performance of the concrete.

Two variations were used for the project; Variation 1 (V1) saw the profile changed by (-10°C, +5°C) with the maximum temperature of V1 was reduced to show a closer representation of the temperatures seen throughout the year rather than just a few days during the summer months (June, July and August). Moreover, the maximum temperature represents temperature seen with the last ten years during the winter months with the minimum temperature reached at certain periods of the season.

Variation 2 (V2) had the maximum temperature reduced and the minimum temperature increased. This temperature variation was selected to represent temperatures seen during milder winter months. Table 7.1 shows the upper and lower limits of the temperature profiles and Figure 7.1 illustrates how the temperature profiles vary from the CEN test.

Table 7.1 Comparison between the upper and lower limits of the two-temperature variation profile with the CEN profile

Temperature Envelope	Upper Limit (°C)	Lower Limit (°C)
CEN	+20.0 ± 4.0	-18.0 ± 4.0
Variation 1 (V1)	+13.0 ± 4.0	-13.0 ± 4.0
Variation 2 (V2)	+18.0 ± 4.0	-8.0 ± 4.0

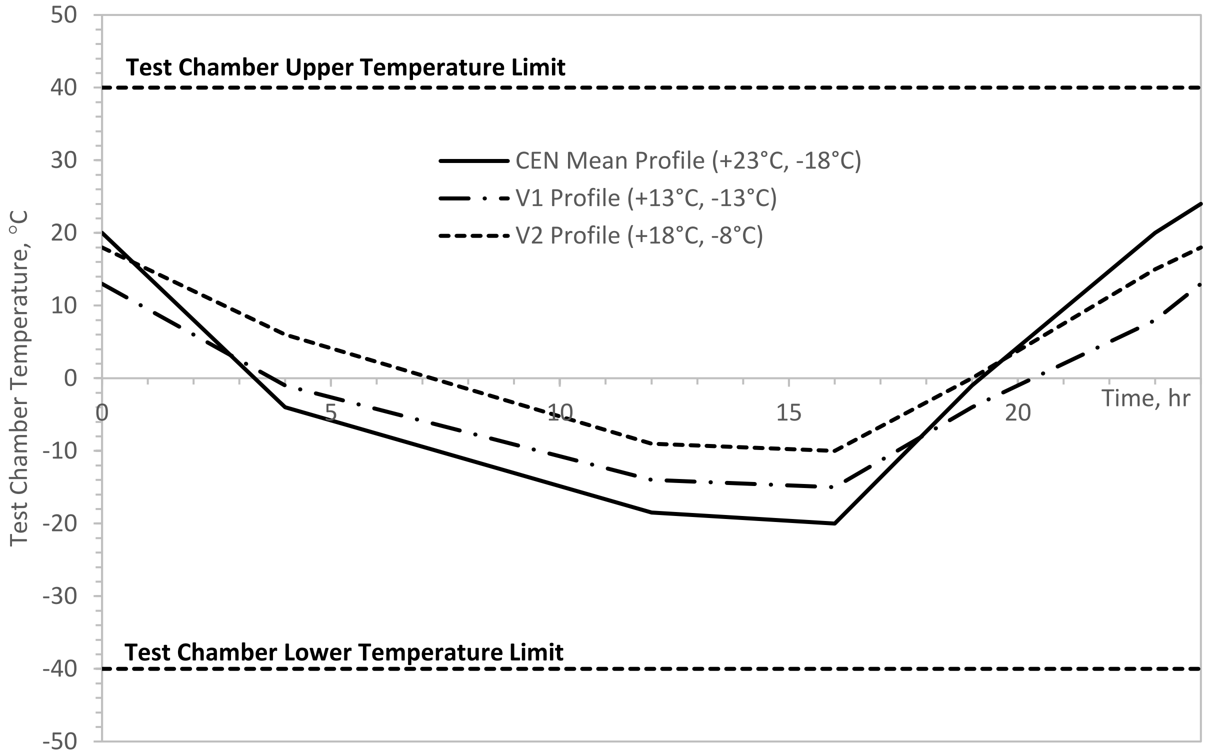


Figure 7.1 Graph illustrating the temperature profile in CEN/TS 12390-9 with different variations in the temperature profile

7.2.1 Temperature Profile Variation 1 (V1)

Figure 7.2 shows the freeze-thaw scaling results for the samples using Variation 1 temperature profile and Table 7.2 tabulates the results showing the rate of deterioration and the scaling criteria in accordance with SS 137244. All the concretes which were non-air entrained did not perform as well compared to the air entrained samples which was expected as without air entrainer the concrete struggles to withstand freeze-thaw attack. The temperature profile changes from +13°C to -13°C from the standard +23°C to -18°C (+10, -5°C) and the results show a significant mass loss for CEM I and CEM II/B-V. The increased mass loss for these two concretes outline that the temperature profile is more effective in testing the concrete's durability. Even though the minimum temperature has increased by 5°C, more damage occurs because the length of time the temperature profile remains at the minimum temperature is longer allowing more water particles to freeze rather than reaching an even lower temperature but remaining there for less time. CEM II/B-V was expected to perform the poorest due to containing fly ash which does not perform well during freeze-thaw especially non-air entrained mixes.

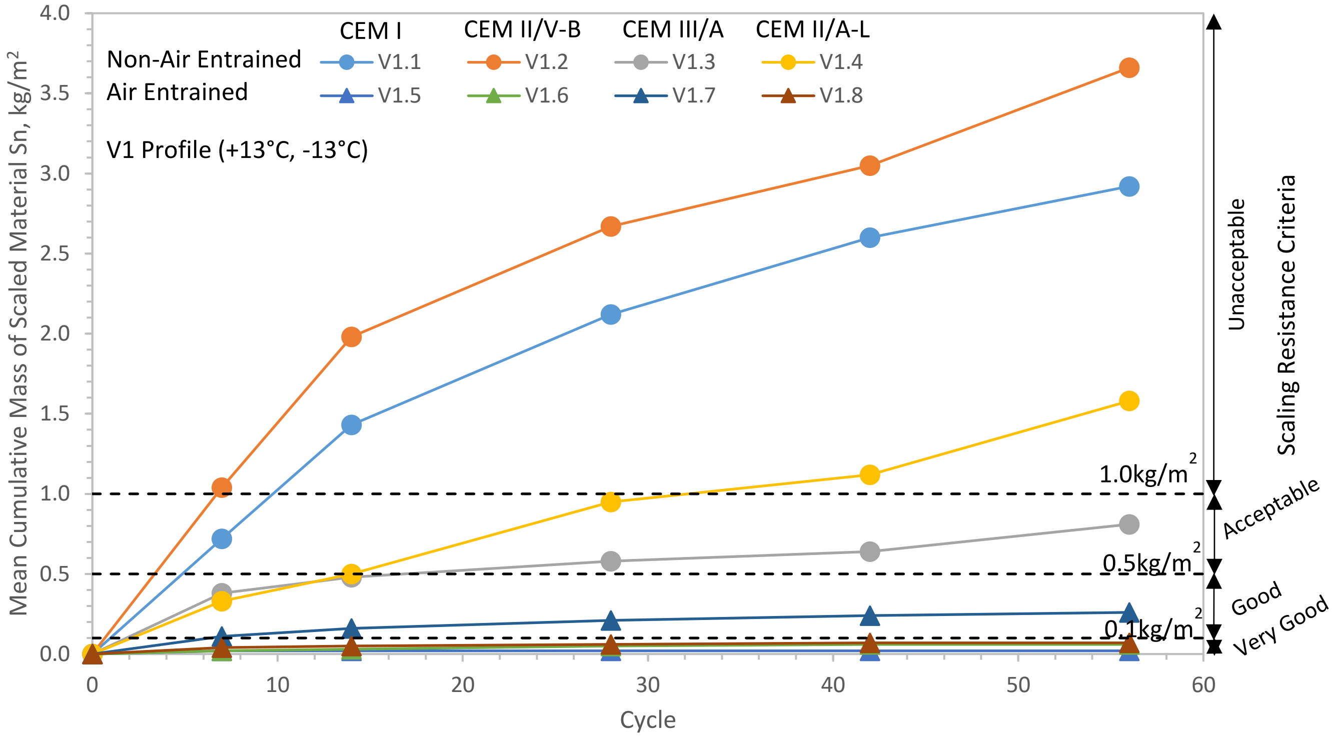


Figure 7.2 Freeze-thaw scaling results of different concretes using Variation 1 temperature profile (+13 °C, -13 °C)

Table 7.2 Scaling criteria results for target strength 40 MPa concretes with different cement types using the first variation of the CEN temperature profile showing the approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m²	Approx. Cycle No. of Limit $Sn \geq 1.0kg/m^2$	Sn_{56}/Sn_{28}	Rate of Deterioration	Scaling Criteria
	Concrete Type	w/c	Air Content, %					
Non-Air Entrained								
V1.1	CEM I	0.54	1.2	2.92	7 – 14	1.38	1.0542ln(x)	Unacceptable
V1.2	CEM II/B-V	0.47	1.5	3.66	0 – 7	1.37	1.1882ln(x)	Unacceptable
V1.3	CEM III/A	0.52	1.3	0.81	na	1.38	0.1851ln(x)	Acceptable
V1.4	CEM II/A-L	0.54	1.1	1.58	28 – 42	1.66	0.5689ln(x)	Unacceptable
Air Entrained								
V1.5	CEM I	0.45	4.7	0.02	na	1.00	0.020ln(x)	Very Good
V1.6	CEM II/B-V	0.4	4.9	0.06	na	1.31	0.0212ln(x)	Very Good
V1.7	CEM III/A	0.44	4.8	0.26	na	1.24	0.0723ln(x)	Acceptable
V1.8	CEM II/A-L	0.45	4.4	0.07	na	1.10	0.0153ln(x)	Very Good

na – Not applicable

CEM I performs nearly as poorly as CEM II/B-V with a high mass loss (2.92 kg/m^2 and 3.66 kg/m^2 respectively). The high mass loss of these two concretes were attributed to the reduction in the maximum temperature. Reducing the temperature from +23°C to +13°C means that it takes less time to reach the maximum temperature, but also reducing the time it takes for the temperature of the concrete to reach below freezing. Moreover, the total time the sample remains below 0°C increases from 16.5 hours for the CEN test to 18 hours. This time increase combined with a reduced temperature envelope (41-degree difference between +23°C and -18C for the CEN test to 26-degree difference) would see a significant increase in the mass loss from the samples.

Although non-air entrained, CEM III/A still meets an *Acceptable* scaling criterion with only a mass loss of 0.81 kg/m^2. CEM II/A-L performs better than CEM I by comparison which was not expected due to limestone addition having no chemical benefits. However, limestone does have finer particles than CEM I so the limestone particles can fit between the CEM I particles reducing the void space and increasing the compressive strength.

Comparing the results for the non-air entrained concrete (Figure 7.3) there were significant differences in the material lost between the CEN test samples and the samples using the Variation 1 temperature profile. The change in the temperature resulted in the total mass loss for the samples increasing by more than 60% (Table 7.3) showing that the variation in the temperature profile details a major increase in the deterioration. Whilst this result is unusual as the lower limit has increased by 5°C, more deterioration has been considered because the temperature remains below freezing for longer enabling more water in the voids to freeze causing further damage to the concrete.

The scaling of the samples from the varied temperature profiles scaled the same way as the bulk mixes (M-mixes) where the material was lost on the test surface and the compressive strengths of the samples were similar by comparison (Figure 7.3). But this did not account for the increase in the scaled material loss compared to the bulk mixes. A 60% increase in the loss was observed relating to the length of time the temperature profile remained below freezing causing more solution to freeze, expand and damage the concrete, and with no air entrainment the concrete would not be able to resist the pressures exerted from the expansion.

For the air entrained samples (Figure 7.4) the results were similar to each other in terms of the mass loss. Although there were differences in the total mass loss (Table 7.3), the overall result was very small compared to the non-air entrained samples. As with the CEN tested samples, the scaling criteria for the varied temperature profile was a minimum *good* or *very good*.

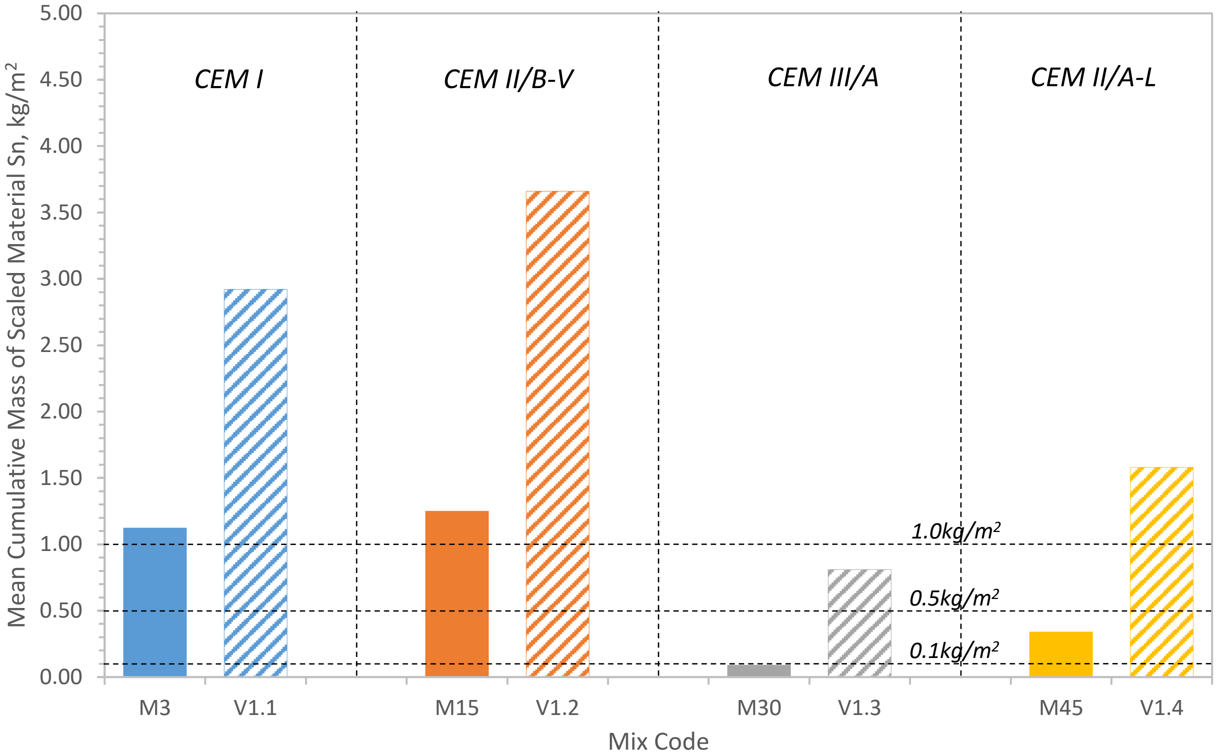


Figure 7.3 Comparison between freeze-thaw scaling results at 56 cycles of different non-air entrained 40MPa concretes using Variation 1 temperature profile (+13°C, -13°C) and the samples using CEN temperature profile (+23°C, -18°C)

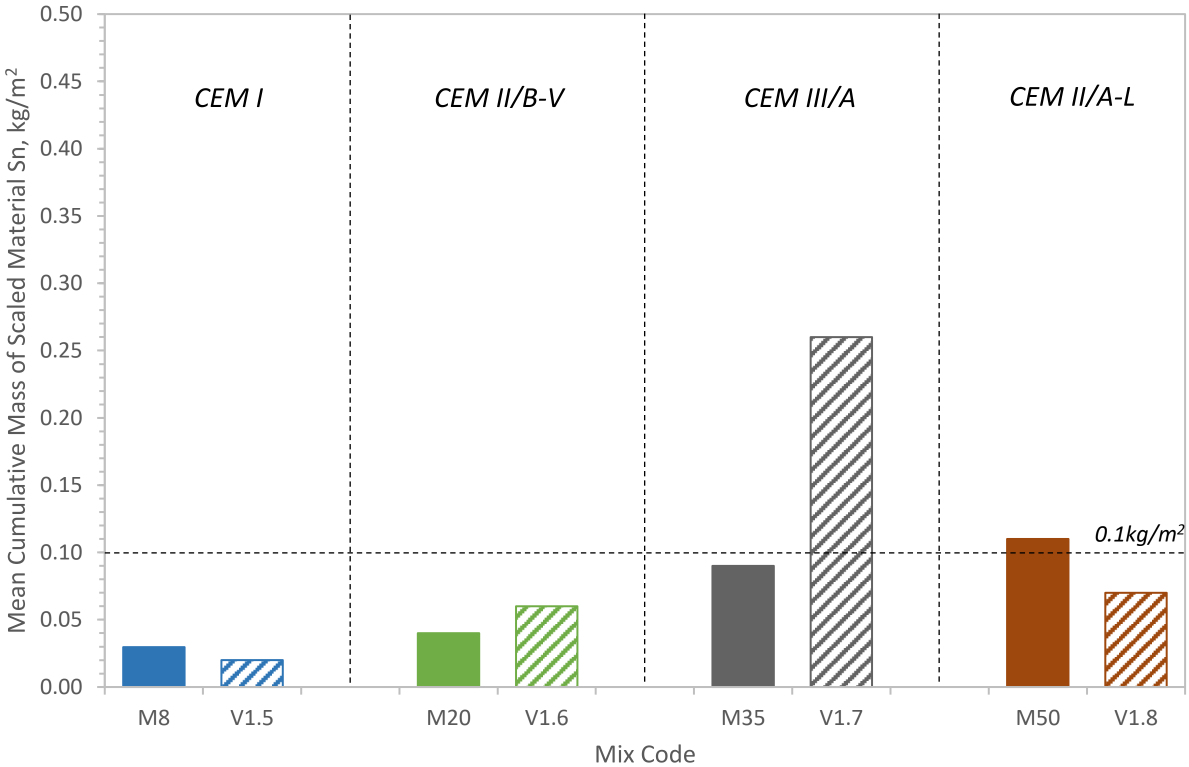


Figure 7.4 Comparison between freeze-thaw scaling results at 56 cycles of different air entrained 40MPa concretes using Variation 1 temperature profile (+13°C, -13°C) and the samples using CEN temperature profile (+23°C, -18°C)

Table 7.3 Comparison between Variation 1 and CEN temperature profiles for both air and non-air entrained concretes with different cement types at 56 cycles

Cement Type	CEN Temperature Profile		Variation 1 Temperature Profile		% Increase in Loss
	Mix Code	Sn, kg/m^2	Mix Code	Sn_{56}, kg/m^2	
Non-air Entrained					
CEM I	M3	1.12	V1.1	2.92	61.6
CEM II/B-V	M15	1.25	V1.2	3.66	65.8
CEM III/A	M30	0.09	V1.3	0.81	88.8
CEM II/A-L	M45	0.34	V1.4	1.58	78.5
Air Entrained					
CEM I	M8	0.03	V1.5	0.02	na
CEM II/B-V	M20	0.04	V1.6	0.06	33.3
CEM III/A	M35	0.09	V1.7	0.26	65.4
CEM II/A-L	M50	0.11	V1.8	0.07	na

7.2.2 Temperature Envelope Variation 2 (V2)

The second variation saw the temperature favour a milder temperature range with the minimum temperature reaching -8°C compared -18°C for the CEN test, and a reduction in the maximum temperature from +23°C to +18°C (-5°C, +10°C). Figure 7.5 shows the freeze-thaw scaling of the samples which were subjected to the second temperature variation and Table 7.4 lists the mix design characteristics, rates of deterioration and scaling rate in accordance with SS 137244. Not only is the maximum temperature higher but the length of time where the temperature remains below 0°C decreases from 16 hours to 12 hours which influences the rate of deterioration.

Using this temperature variation saw both the non-air and air entrained samples gain a *very good* freeze-thaw scaling resistance with the exception being V2.2 (non-air entrained CEM II/B-V) gain an *acceptable* rating but remaining below 1.0 kg/m^2. As shown from Figure 7.5 and Table 7.4, the air entrained samples had zero material loss during the testing showing that these samples achieve a *very good* scaling rating. However, these samples may have the classification of being *very good*, but it is also related to how harsh the temperature profile is. Compared to V1, V2 does not subject the concrete to harsh enough temperature fluctuations. Whilst V1 does subject the concrete to better representative temperatures than the CEN test, V2 is better a representation of real life but not enough to produce damage. The temperature profile should be harsh enough to stress the samples under freeze-thaw conditions but without decimating the samples to failure, thus, increasing the quantity of either CEM I or air entrainer therefore, increasing CO_2.

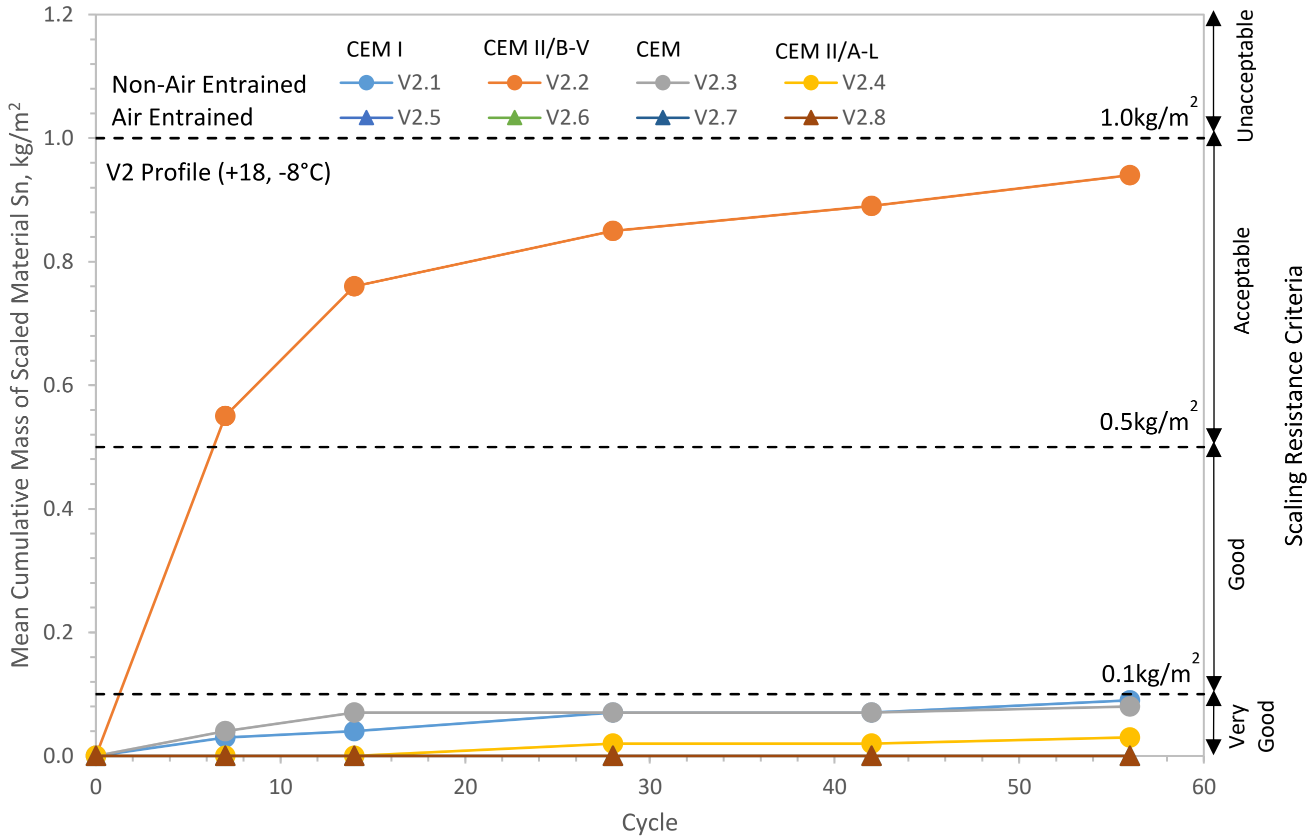


Figure 7.5 Freeze-thaw scaling results of different non-air and air entrained 40 MPa concretes using Variation 2 temperature profile (+18, -8°C)

Table 7.4 Scaling criteria results for different concretes using the second variation of the CEN temperature profile showing the approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	**Mix Characteristics**			**Sn_{56}, kg/m^2**	**Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2**	**Sn_{56}/Sn_{28}**	**Rate of Deterioration**	**Scaling Criteria**
	Concrete Type	**w/c**	**Air Content, %**					
Non-Air Entrained								
V2.1	CEM I	0.54	1.3	0.09	na	1.29	0.0281ln(x)	Very Good
V2.2	CEM II/B-V	0.47	1.6	0.94	na	1.11	0.1772ln(x)	Acceptable
V2.3	CEM III/A	0.52	1.1	0.08	na	1.14	0.0156ln(x)	Very Good
V2.4	CEM II/A-L	0.54	0.9	0.03	na	1.50	0.0149ln(x)	Very Good
Air Entrained								
V2.5	CEM I	0.45	4.9	0.0	na	0.0	0.0	Very Good
V2.6	CEM II/B-V	0.4	4.5	0.0	na	0.0	0.0	Very Good
V2.7	CEM III/A	0.44	4.2	0.0	na	0.0	0.0	Very Good
V2.8	CEM II/A-L	0.45	4.6	0.0	na	0.0	0.0	Very Good

The results regarding the air entrained samples, these showed to have a high resilience to freeze-thaw attack, but this would be linked to increase in the minimum temperature. Although the minimum temperature was increased to represent the temperature concrete would typically be subjected to, it resulted in the concretes being able to withstand damaging effects not giving a clear indication on the freeze-thaw effects. This would be because of the temperature not remaining long enough below zero degrees and majority of the temperature remaining above zero degrees.

7.2.3 Summary of Changing Temperature Envelopes

The CEN test temperature profile creates a temperature envelope rarely seen in the UK especially freezing temperatures where the lower limit tests between -22°C to -16°C. The two variations show different options for replacing the current standard whilst still providing a temperature range that tests the concretes durability. V1 showed to be the more promising envelope of the two as the temperature difference between the upper and lower limit is reduced from 41°C to 26°C increasing the length of time the concrete is under freezing temperatures, hence, allowing for realistic deterioration.

Whereas, V2 provides a more realistic temperature profile observed in Scotland with +18°C being the average maximum and -8°C the average minimum. However, this profile has issues in regards to testing as the results showed that very little deterioration happened compared to CEN and Variation profiles leading to the conclusion that either the concrete (both air and non-air entrained groups) are acceptable for freeze-thaw conditions as all achieved an *Acceptable* scaling rating or the temperature profile is not extreme enough to cause long term effects. Either option could be argued however, it is in the author's opinion that the former would be the reason. Since there is not a drop in temperature within a short period the concrete would be tested as though it were a real concrete element being tested.

Overall it is considered that temperature Variation 1 would be the preferred option of the two as it provides a temperature regime that is representative of the current climate compared to the CEN test and even though the is only 5°C between the lower limits of the profile compared to the CEN profile, -13°C is still observed in the current climate.

7.3 Testing Cast Surface and the Addition of the Scaled Material from the Sides and Base

7.3.1 Comparison Influence of Testing Cast Surface Compared to CEN Tested Concretes

CEN/TS 12390-9 tests the concrete for freeze-thaw scaling but only looks at the internal bulk concrete where the concrete has higher strength rather than looking at both internal and external layers. Understandably, the internal surface is tested so that if the test surface does not meet the scaling criteria then the sample would not be suitable. Extensive testing was conducted in Chapter 5 analysing strengths, cement types, replacement content and air content and found that concrete which was air entrained performed well in freeze-thaw. Again, this was based on the internal surface. Using the same concretes from the bulk casting (the untested half) the sample were flipped and the cast surfaces (CS) were tested at the same age and thickness instead as these surfaces would be exposed to the environment. It should be noted that there are imperfections on the surface shown in Figure 7.6. Despite best efforts to remove the entrapped air voids from the concrete, it is very difficult to remove all of them. Whilst it is plausible that these imperfections will increase the likelihood of deterioration, it still shows the realistic surface which is seen on a concrete element allowing improved representation of real time.

Figure 7.7 shows the cumulative mass of scaled material of the cast surface for different concrete types and Table 7.5 outlines the rate of deterioration and scaling criteria. From the results, the concretes which have a certain replacement content and are non-air entrained do not meet the acceptable scaling criteria (<1.0 kg/m^2). However, CEM I (M3$_{cs}$) achieves a *Good* scaling rating with the mass loss being less than 0.5 kg/m^2. Similar to CEM I, all the concretes which are air entrained achieve a good criteria rating.

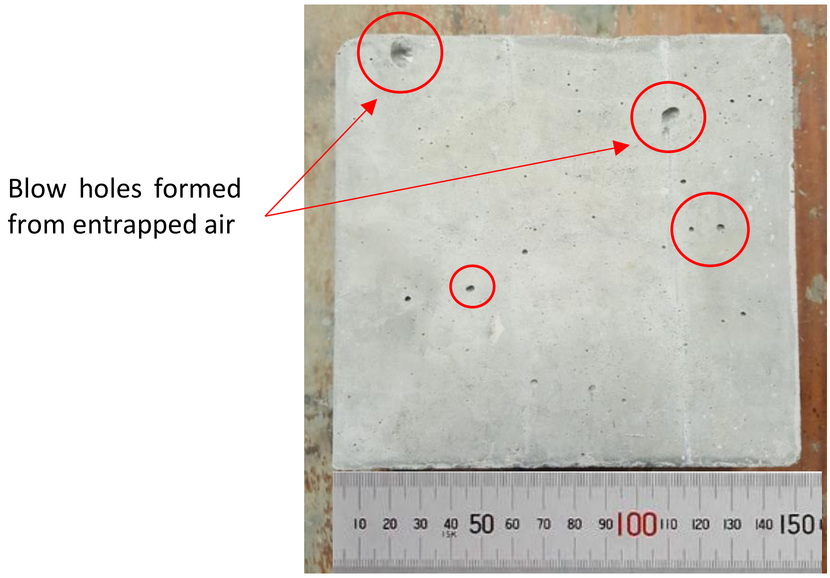


Figure 7.6 Image showing the cast surface of the concrete which was the test surface for freeze-thaw testing with entrapped air voids (circled) possibly contributing to the deterioration of the test surface

Comparing the cast surface samples to the CEN test surface results in Figure 7.8 and Figure 7.9, there were observed differences in the mass loss. Both the air and non-air entrained samples show higher scaling for the cast surface test compared to the CEN surface except for M3 which had a higher mass loss. The increase in the mass loss is due to the weaker concrete section on the outside of the sample. Referring to Figure 2.5, Kreijger (1990) determined that once a concrete element had been cast the cement paste would divide into different layers with the outer layer (cement skin) being the weakest. From this the results show this differentiation of layers to be true as the results show more scaled material from the cast surface than the CEN tested samples.

Figure 7.10 and Figure 7.11 show the deterioration after (a) 7 cycles and (b) 56 cycles for CEM III/A concretes which have a target strength of 40 MPa for both air and non-air entrained samples. The non-air entrained sample shown to have increased damage even after the first test age (7cycles) with majority of the top layer (Figure 2.5) having scaled off. The scaling continues throughout the test with less material loss. Same can be said about the air entrained sample.

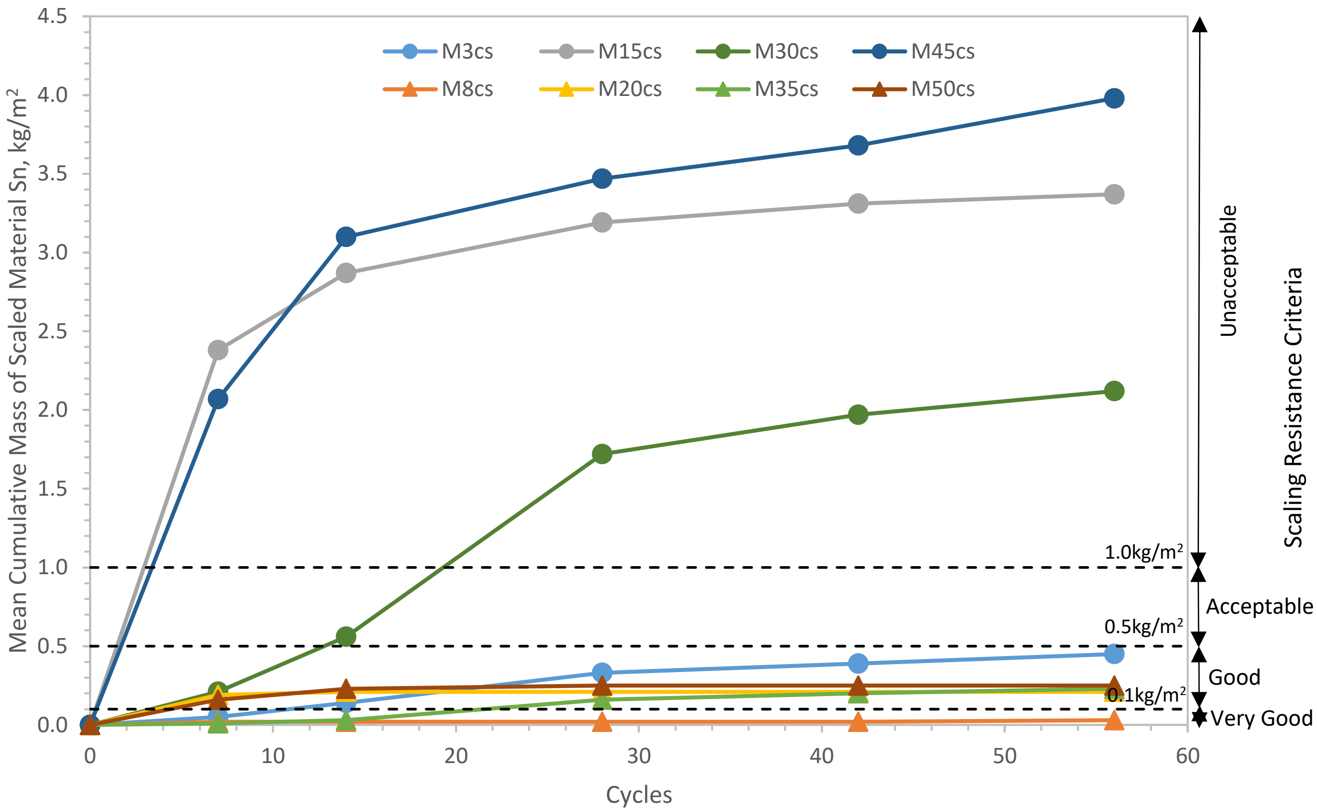


Figure 7.7 Freeze-thaw scaling results for cast surface testing of different cement types both air and non-air entrained showing the scaling resistance criteria

Table 7.5 Cast surface scaling criteria results for different concretes showing the approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	Mix Characteristics			Sn_{56}, kg/m²	Approx. Cycle No. of Limit Sn≥1.0kg/m²	Sn_{56}/ Sn_{28}	Rate of Deterioration	Scaling Criteria
	Concrete Type	w/c	Air Content, %					
Non-Air Entrained								
$M3_{cs}$	CEM I	0.54	0.9	0.45	na	1.36	0.1998ln(x)	Good
$M15_{cs}$	CEM II/B-V	0.47	1.3	3.37	0 – 7	1.06	0.4748ln(x)	Unacceptable
$M30_{cs}$	CEM III/A	0.52	1.1	2.12	14 – 28	1.23	1.0088ln(x)	Unacceptable
$M45_{cs}$	CEM II/A-L	0.54	1.2	3.98	0 – 7	1.15	0.8512ln(x)	Unacceptable
Air Entrained								
$M8_{cs}$	CEM I	0.45	4.8	0.03	na	1.5	0.0031ln(x)	Very Good
$M20_{cs}$	CEM II/B-V	0.4	4.2	0.21	na	1.0	0.0083ln(x)	Good
$M35_{cs}$	CEM III/A	0.44	4.3	0.23	na	1.44	0.1154ln(x)	Good
$M50_{cs}$	CEM II/A-L	0.45	4.6	0.25	na	1.0	0.0410ln(x)	Good

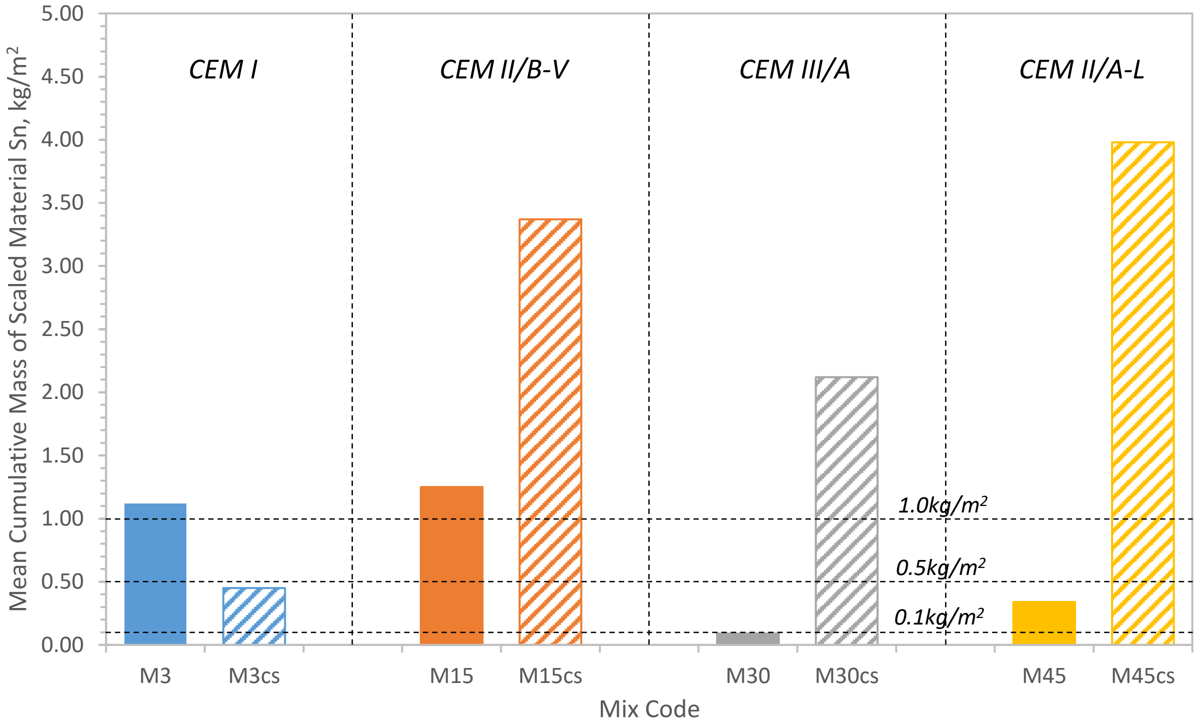


Figure 7.8 Comparison between cast surface and CEN surface tested for non-air entrained 40MPa concretes with different cement types

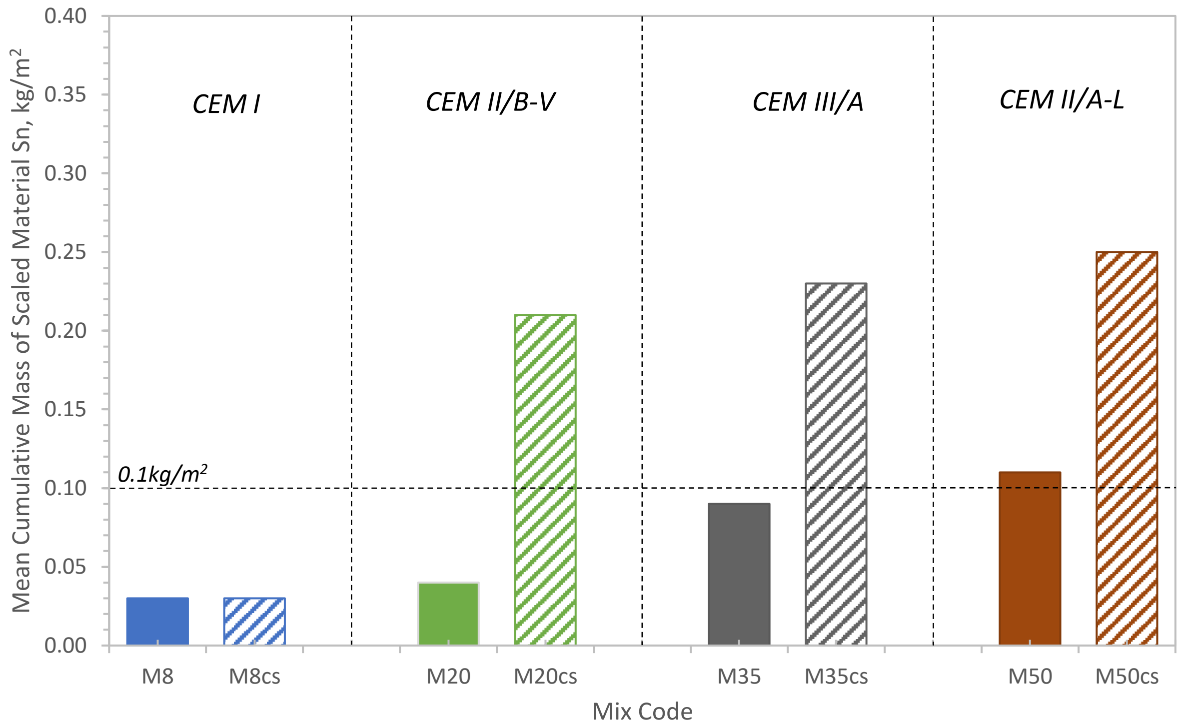


Figure 7.9 Comparison between cast surface and CEN surface tested for air entrained 40MPa concretes with different cement types

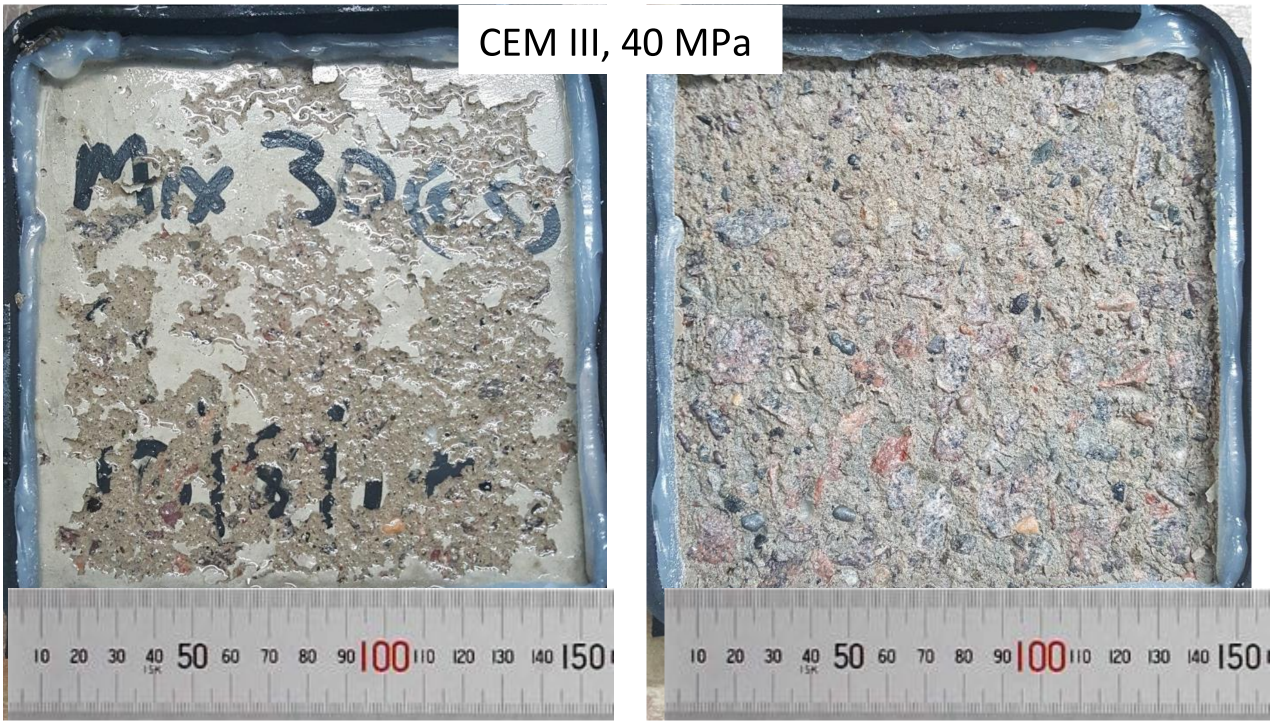


Figure 7.10 Scaling of the concretes cast surface during the freeze-thaw test of Mix 30_{cs} at (a) 7 cycles and (b) 56 cycles

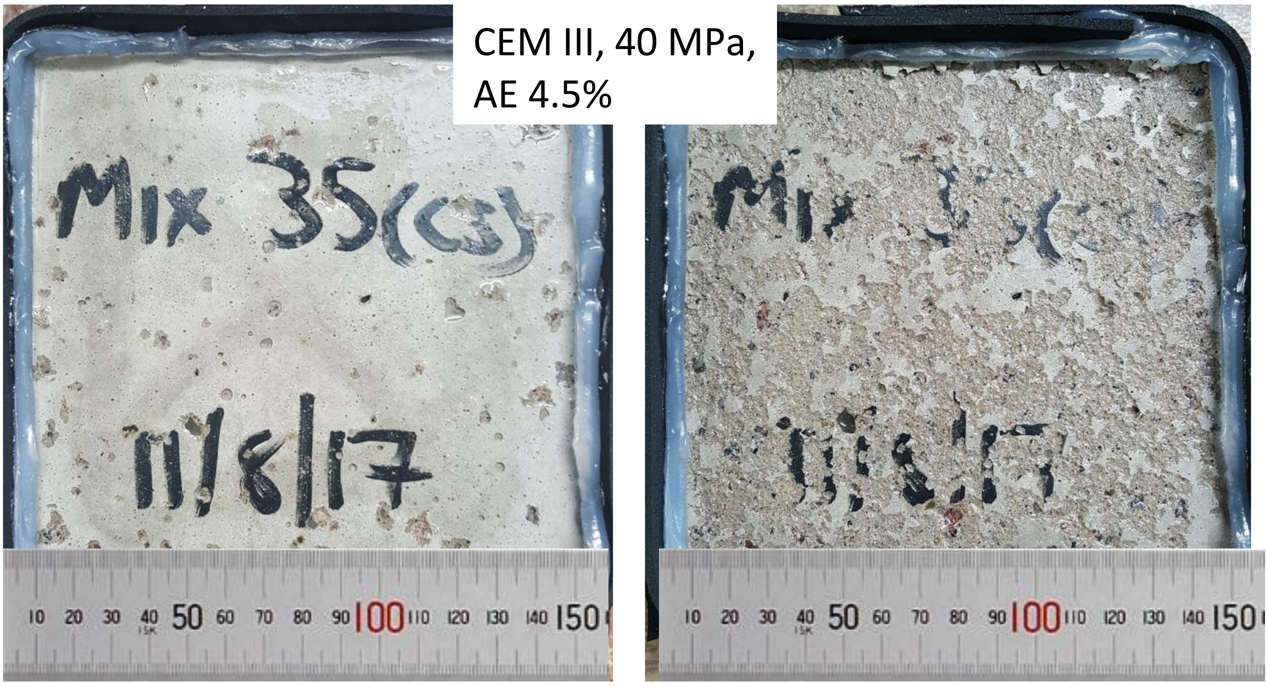


Figure 7.11 Scaling of the concretes cast surface during the freeze-thaw test of Mix 35_{cs} at (a) 7 cycles and (b) 56 cycles

Although less material scaled off compared to the non-air entrained sample, after 56 cycles, there was nearly as much deterioration. Coinciding with the research from Kreijger (1990) and the scaling results, it can be assumed that even with the inclusion of air entrainment in the concrete, there is still scaling occurring due to the poor outer layer of the concrete make-up. The image in Figure 7.10a shows some of the concrete still intact which could be a result of the pen markings on the surface. If this were the case then all areas which had pen written on the top would remain in place and what would be seen would be solid concrete outline of the lettering, however, as shown the pen markings have partially scaled off.

7.3.2 Influence of the Additional Scaling from the Base and Side on the Total Mass of Scaled Material

One aspect of the freeze-thaw test which is not considered is the influence of the additional scaled material from the sides and base of the samples. Although the standard does not mention the inclusion of scaled material from other surfaces, it was investigated as to how much the cumulative mass loss of scaled material would be affected with the additional material (Figure 7.12). In the real world, concrete elements that are exposed to the environment are subject to various deterioration mechanisms and it is not just one face that is open but rather all are affected in some form. Sometimes there are some faces are covered of hidden from view then these may be hiding scaled material or deterioration not in obvious view.

Figure 7.12 CEM I non-air entrained sample showing scaled material from the sides and base

The sides and base are sealed off with rubber wrap to reduce temperature fluctuations within the sample and to reduce the loss of the saline solution down the sides with the constant expanding and contracting of the sample and the silicone sealant. The expansion and contraction of the silicone causes the surface of the concrete to be pulled away from the sample which induces cracking around the edges leading to the solution to dissipate. Moreover, with ponding on the test surface there is infiltration from the solution plus the de-ionised saturation during preparation for the test, fill the voids along the edges of the sample and once freezing has occurred, the surface concrete layer has scaled as show in Figure 7.12.

During the freeze-thaw test minimal scaling may occur on the surface meaning the concrete could potentially achieve a *Good* scaling rating. If this were the case, then examination of the sides and base needs to be conducted to assess whether the sample does withstand freeze-thaw attack. Table 7.6 lists a selection of concretes tested for freeze-thaw showing the Sn_{56} values before and after adding the scaled material from the sides and base.

Table 7.6 Range of concretes of different cement types and strengths showing Sn_{56} before and after the additional scaled material were added

Mix Code	Mix Characteristics		Before		Sn_{56} of Sides and Base, kg/m^2	After	
	Concrete Type	Strength, MPa	Sn_{56}, kg/m^2	Scaling Rating		Sn_{56}, kg/m^2	Scaling Rating
Non-Air Entrained							
M2	CEM I	30	1.27	Unacceptable	1.82	3.09	Unacceptable
M4		50	0.87	Acceptable	0.02	0.89	Acceptable
M14	CEM II/B-V	30	2.00	Unacceptable	33.98	35.98	Unacceptable
M16		50	1.26	Unacceptable	2.13	3.39	Unacceptable
M29	CEM III/A	30	0.09	Very Good	0.02	0.11	Good
M31		50	0.07	Very Good	0.01	0.09	Very Good
M44	CEM II/A-L	30	1.95	Unacceptable	0.43	2.38	Unacceptable
M46		50	0.36	Good	0.13	0.49	Good
Air Entrained							
M7	CEM I	30	0.26	Good	0.01	0.27	Good
M9		50	0.00	Very Good	0.01	0.01	Very Good
M19	CEM II/B-V	30	0.08	Very Good	0.07	0.15	Good
M21		50	0.02	Very Good	0.01	0.03	Very Good
M34	CEM III/A	30	0.50	Good	0.06	0.56	Acceptable
M36		50	0.09	Very Good	0.03	0.12	Good
M49	CEM II/A-L	30	0.18	Good	0.03	0.21	Good
M51		50	0.07	Very Good	0.01	0.08	Very Good

The influence of the additional scaled material is dependent on the strength and cement type. Typically, the higher the strength, the less material is lost from scaling. Previous testing (Chapter 5) has seen CEM II/B-V concretes lose the most material for both air entrained and non-air entrained and CEM III/A losing approximately the same material for both air entrained and non-air entrained concretes. Table 7.6 shows how the additional scaled material influences the final Sn_{56} value. Comparing the non-air entrained concretes, there is definite changes in the total scaling before and after the additional material. Most of the samples had already surpassed the 1.0 kg/m^2 so the extra material would only be adding to the already *unacceptable* concrete.

The air entrained concretes are influenced by the additional material more than the non-air entrained as the additional material has the capability to affect the scaling criteria due to how close the performance ratings are to each other, especially the *very good* and *good* scaling ratings.

Although it is understood that the CEN test focuses on one test surface to determine the performance capability, the addition of the scaled material from the sides and base has been shown to properly evaluate how well the concrete performs. As previously explained in Section 7.3.1, the cast surface of the concrete is the poorest and should be the surface considered for testing to give an accurate representation of freeze-thaw in real time. The same can be said for testing of the sides and base. When concrete members are subjected to freeze-thaw attack it is not just one surface/side of the member, but all sides and the addition of the sides provides a total value of the scaled material which can then be used to determine a suitable strength and cement type for each concrete.

7.4 Influence of Varied NaCl Concentration on the Concrete Surface

The increase in the NaCl concentration is a replication of the higher de-icing salt levels applied to certain horizontal surfaces continuously throughout a particular period and increasing the concentration was to best replicate those seen during the winter months on the Scottish road network. CEN/TS 12390-9 tests the concrete samples with 3% NaCl solution equating to approximately 90 g/m^2 in real terms observed on the roads with two applications daily during heavy snow. Increasing the concentration to 6% (178 g/m^2), 9% (268 g/m^2) and 12% (357 g/m^2) was to show further applications on top what had already been applied increasing the concentration and continual spray from concentrated ponding on the surface.

The influence of the concentration was tested to determine whether the concrete deterioration is caused by the increase in NaCl levels and these were compared to the CEN test to investigate how damaging the NaCl concentration can be. The testing showed zero scaled material from the samples from all three (6%, 9% and 12%) concentrations meaning the samples effectively performed very well during the freeze-thaw scaling test. Although no surface scaling had taken place, the samples had started to show cracking externally. Figure 7.13 shows images of surface cracking on CEM I concretes with NaCl concentrations (a) 9% and (b) 12%. What was observed was the increase in the NaCl concentration also increased the amount of cracking, enough to prevent the sample to remain test viable so the outcome of the test was as follows:

- 3% saw scaling of the test surface;
- 6% saw minor surface cracks but not enough for the solution to drain away;
- 9% saw a high number of minor cracks (up to 1mm) throughout the concrete, enough to prevent the test from continuing and;
- 12% saw a small number of major cracks (measuring up to 3mm in width) throughout the concrete causing large pieces to come away so easily.

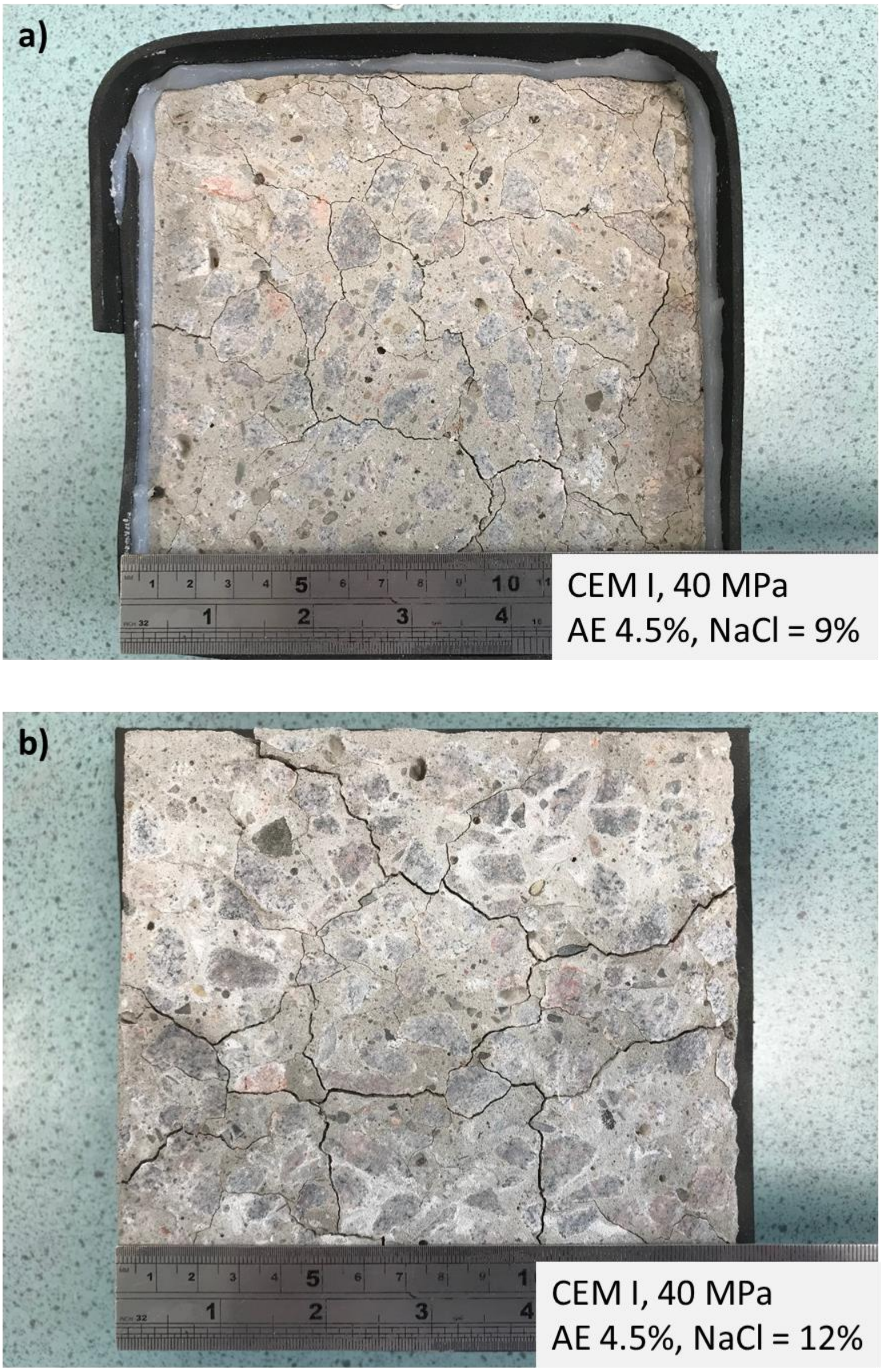


Figure 7.13 Concretes exposed to 56 cycles with higher NaCl solutions of (a) 9% and (b) 12%. No surface scaling is apparent however cracking is evident

Analysis was conducted using the micro-CT scanner to understand how damaging the NaCl concentration was on the concrete. Visually, cracks were forming on the external surface which was a result of an internal freeze-thaw mechanism. During the test the saline solution would infiltrate the concrete and begin to saturate the voids. As the temperature increased the water from the solution would evaporate leaving the NaCl particles.

This continuous drying with further applications of solution to the surface caused enough NaCl to build up inside the voids to invoke pressure against the void walls and the further applications of the solution along with the underlying NaCl build up caused the pressure to crack the concrete, and surface cracking became visible. This opens the question as to why the outer layer does not scale with the high NaCl concentration.

Figure 7.14 and Figure 7.15 show the samples which was analysed using micro-CT image. Comparing the two samples (9% and 12%) there were observed differences between the surface cracking. The sample which had 9% solution shows defined cracking throughout the concrete particularly around the edges of the samples. Whilst the concrete with 12% solution had less surface cracking overall however the cracks were more defined and more widely spaced.

Reviewing the photographs and CT images, it was identified that there was minimal scaling on the test surface however there was major cracking throughout the concrete sample. Moreover, there was significantly larger cracking at the bottom of the sample which progressed upwards reducing in width at the top suggesting that the saline solution is not freezing due to the high NaCl concentrations. Instead, the water molecules at the bottom have frozen causing cracking which has travelled up the sample.

NaCl deposition occurred at the top of the sample would prevent the solution from freezing. Further observations indicate that with the NaCl particles being deposited, the freeze-thaw deterioration method changed from freeze-thaw salt scaling to internal freeze-thaw which infers that the deterioration mechanism would have changed from surface scaling to internal freeze-thaw which may detail that both mechanisms were deteriorating the concrete simultaneously rather than one or the other.

Whilst it is understood that the results show the possibility of two mechanisms, since there was no scaling of the test surface then a salt scaling mechanism would not have deteriorated the concrete stipulating that there was only one mechanism deteriorating the concrete. What has been seen from previous testing using the standardised 3% NaCl concentration were that test surfaces were subjected to scaling material loss but no surfacing cracking, however, as the NaCl concentration increases the amount of scaling reduced and the depth of cracking increases. This indicates that there was a single mechanism which was influenced by the NaCl in the solution causing very little scaling but having significant effects on the internal structure.

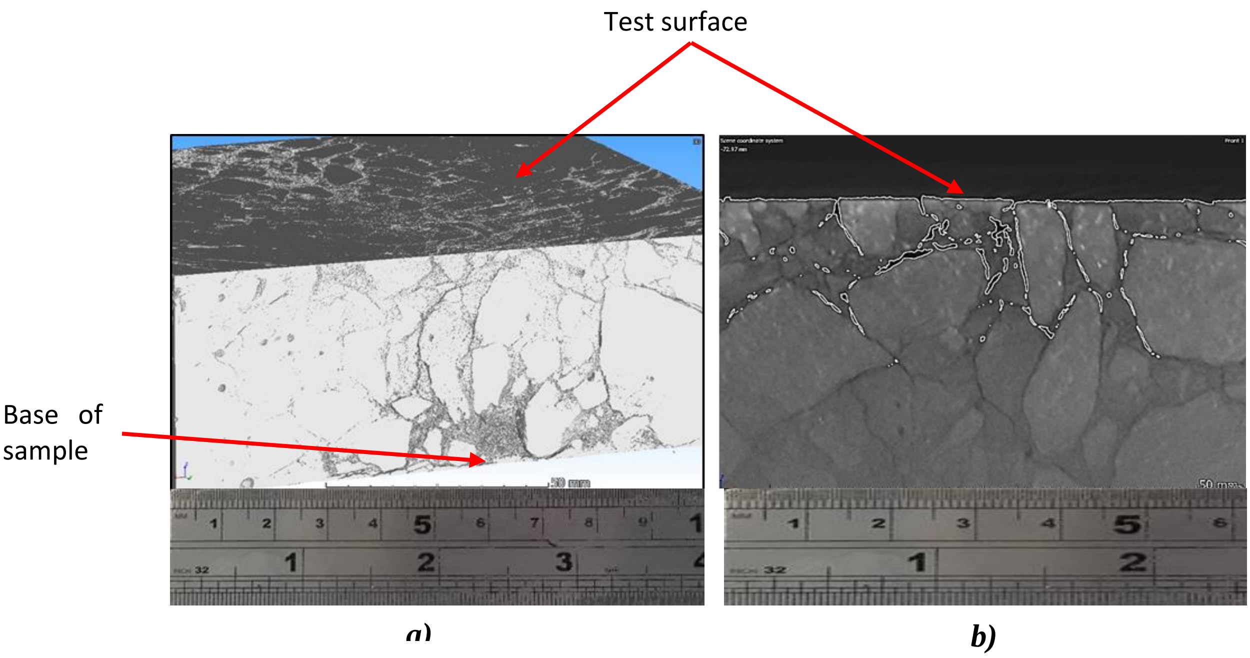


Figure 7.14 µCT scan through CEM I, 40 MPa concrete with AE and increased NaCl test solution of 9%. (a) slice through image showing internal cracking throughout centre of sample, (b) focus on near surface void formation and internal cracking.

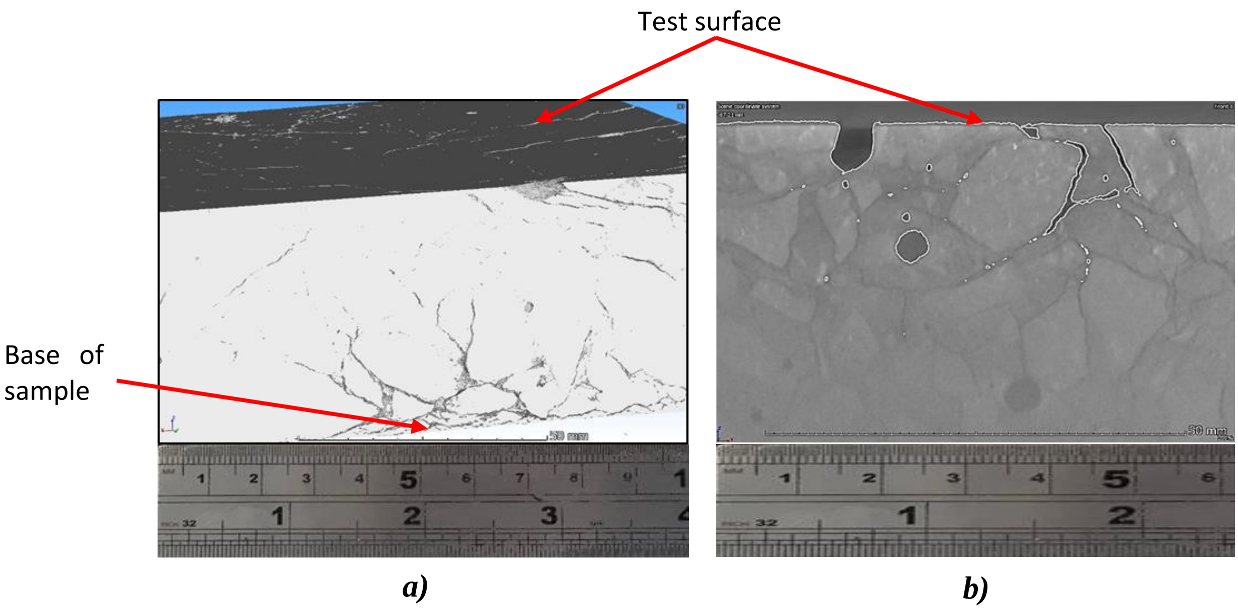


Figure 7.15 µCT scan through CEM I, 40 MPa concrete with AE and increased NaCl test solution of 12%. (a) slice through image showing internal cracking throughout centre of sample, (b) focus on near surface void formation and internal cracking.

It is in the author's opinion that with the higher NaCl concentration created a viscous solution it prevents most of the NaCl from infiltrating the concrete microstructure although there was still a small amount moving through the internal structure mainly comprising of water molecules.

This leads to the idea that the mechanism changes during the test. Initially, the mechanism starts as freeze-thaw salt scaling on the test surface then changes to internal freeze-thaw damage through the concrete. This was observed when the NaCl concentration increased, it prevented the surface solution from freezing though the cracking was more pronounced. This leads to the idea that the NaCl concentration decreases as the solution infiltrates the concrete as there is evidence that the concrete is cracking from the base towards the test surface.

During the test, the samples would be 'topped up' with solution to ensure the concrete was continually subjected to a solution that was freezing and thawing. This would enable the 'diluted' solution (whereby majority of NaCl particles would be deposited at the top leaving a small amount to move through the sample) to infiltrate further into the concrete with every cycle and with further top ups. Since there was no scaling observed on the test surface due to the high NaCl concentration, then it could be a result of internal freeze-thaw resulting from NaCl, hence, crystallisation pressure from the additional NaCl. Had there been scaling of the test surface then the mechanism would be different, possibly a combination of two mechanisms working in tandem to damage the concrete surface and internal structure simultaneously.

The deterioration observed show that over a certain duration the type of deterioration which affects the concrete surface is dictated by the NaCl concentration. From the damage seen, there is a consideration that the NaCl concentration influences the type of deterioration. CEN/TS 12390-9 test method reviews the loss of material by way of surface scaling whereas the ASTM C666 test method looks at how the internal structure is damaged by freeze-thaw, two methods looking at different areas of the concrete sample. However, in the field it can be shown that they in fact work in tandem with one another with the increase in the NaCl level. It would appear from the data that the level of NaCl concentration determines which deterioration mechanism would occur.

As stated with each increase in the NaCl concentration there is a change on how it damages the concrete sample. From the results it shows that for a concrete subjected to a 3% concentration whereby there was surface scaling and with increasing concentration the amount of scaled material decreases and there was an increase in the cracking observed.

7.5 Influence of Carbonation on Freeze-Thaw Test Performance

Carbonation is known to have significant durability implications in reinforced concrete but what needs to be considered is the influence of multiple durability factors. Many studies have been conducted looking at various factors independently of each other and not done together. This section analyses the effects of freeze-thaw testing of carbonated concrete on the split surface (as per the CEN/TS 12390-9 test) with different cement types both air and non-air entrained to determine the influence carbonation has on the freeze-thaw performance.

A series of concretes were carbonated using the accelerated carbonation method, prEN 12390-10 (BSi, 2015) for 5 weeks was considered to be long enough for carbonation to achieve a significant depth, extending the freeze-thaw testing procedure from 12 weeks, where 4 weeks were used for preparation of the samples and 8 weeks of freeze-thaw testing, to 17 weeks with carbonation. The resultant carbonation depths were recorded in Table 7.7. Alternatively, the samples could have been placed into the chamber until a target depth was reached, however, using this method would not replicate the affects seen in real time where concrete elements would be subjected to the same level of carbonation (albeit each country would have different CO_2 emissions). This way it can be understood as to how the concrete's durability regarding cement type and compressive strength with the same test duration influences the freeze-thaw performance.

Table 7.7 Carbonation depth of concrete samples every week for 5 weeks for 150mm specimens

Mix Code	Cement Type	28-day Compressive Strength, MPa	Week 1	Week 2	Week 3	Week 4	Week 5	Carbonation rate, k, mm/d$^{0.5}$
			mm					
Non-Air Entrained								
CN1	CEM I	49.3	2.0	3.7	4.7	6.3	7.3	1.057
CN2	CEM II/B-V	41.0	6.2	8.1	9.5	11.0	14.5	1.546
CN3	CEM III/A	40.6	4.6	6.4	8.2	10.4	10.6	1.295
CN4	CEM II/A-L	36.5	5.5	7.0	7.8	10.7	12.2	1.363
Air Entrained								
CN5	CEM I	48.4	3.1	3.9	4.4	5.5	6.1	0.608
CN6	CEM II/B-V	38.7	5.7	7.5	8.3	11.0	12.4	1.348
CN7	CEM III/A	42.5	4.2	4.7	5.2	7.1	8.7	0.903
CN8	CEM II/A-L	38.7	3.9	5.5	6.5	7.9	8.2	0.887

As shown in Table 7.7, CEM I had the least carbonated depth whilst CEM II/B-V is shown to have the highest carbonated depth for both air and non-air entrained samples. What is observed is all the samples that are air entrained have a lower carbonation depth compared to their non-air entrained counterparts. Figure 7.16 shows the mean cumulative carbonation depths over the 5 weeks. It is unclear why there is a reduction in the carbonation depth when the concrete is air entrained. A study conducted by Younsi, et al. (2011) suggested that the addition of air entraining admixture reduces the viscosity of the concrete, making it more workable which increased the early age strength compared to reducing the water which made the concrete highly viscous. The author has considered it is either the microbubbles have provided additional protection from the carbonation or with the higher cement content to accommodate air entrainment, this has increased the paste density reducing the carbonation rate, or it is a combination of both. The latter of the two options being the more probable as the additional cement provides a denser concrete despite the air entrainment.

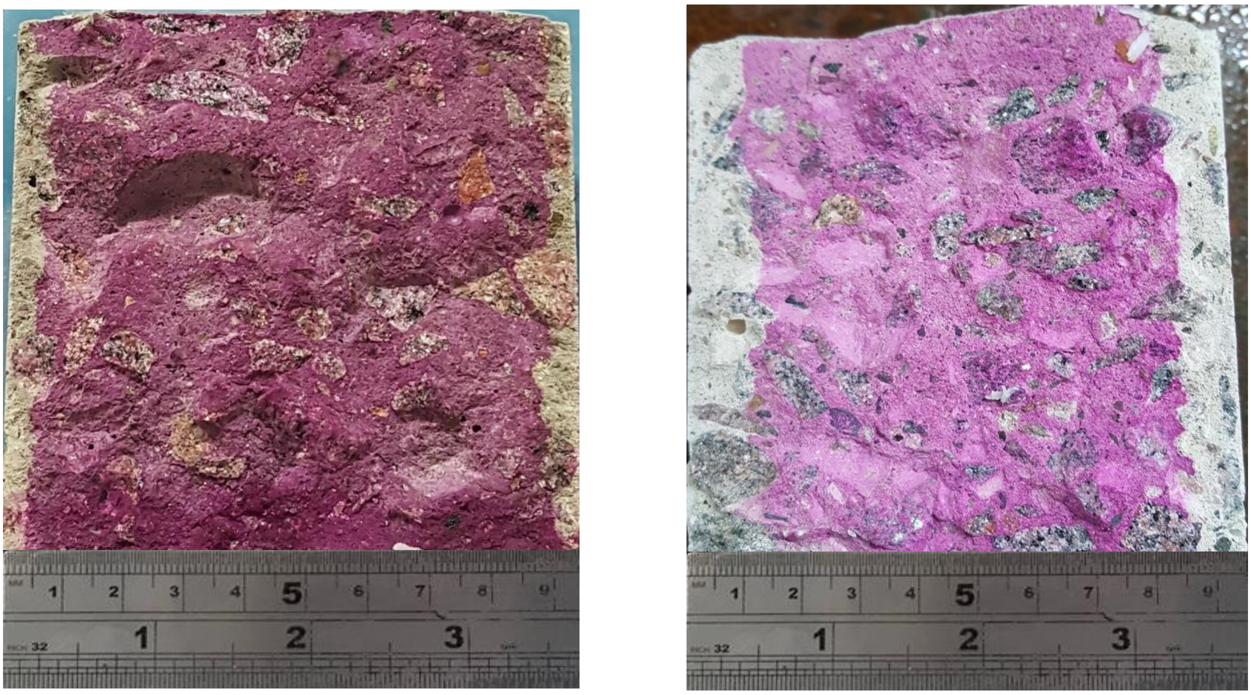


Figure 7.16 Carbonation depths for 40 MPa CEM II/B-V air entrained control concrete at (a) 7 days and (b) 35 days

Once the samples had been carbonated, they were placed into the freeze-thaw chamber for 56 cycles (56 days) and tested in accordance with CEN/TS 12390-9. Figure 7.17 shows the scaling results for the carbonated concrete and the rate of deterioration and scaling criteria tabulated in Table 7.8. As the figure shows, all the non-air entrained concretes have a scaling rating which was unacceptable as the total mass loss was more than 1.0kg/m^2, especially CEM II/B-V and CEM II/A-L both of which were more than 10 times over the maximum allowance. On the other hand, apart from CEM III/A which was only slightly over the limit, all the air entrained samples remained in the acceptable or better ranges. The difference between the air and non-air entrained samples is hugely significant as it shows that the AEA provides a form of protection once it has been carbonated. Figure 7.18 shows the freeze-thaw scaling results for the non-carbonated samples and the rate of deterioration equations and scaling criteria are tabulated in Table 7.9. In comparison the non-carbonated did not scale nearly as much as the carbonated samples.

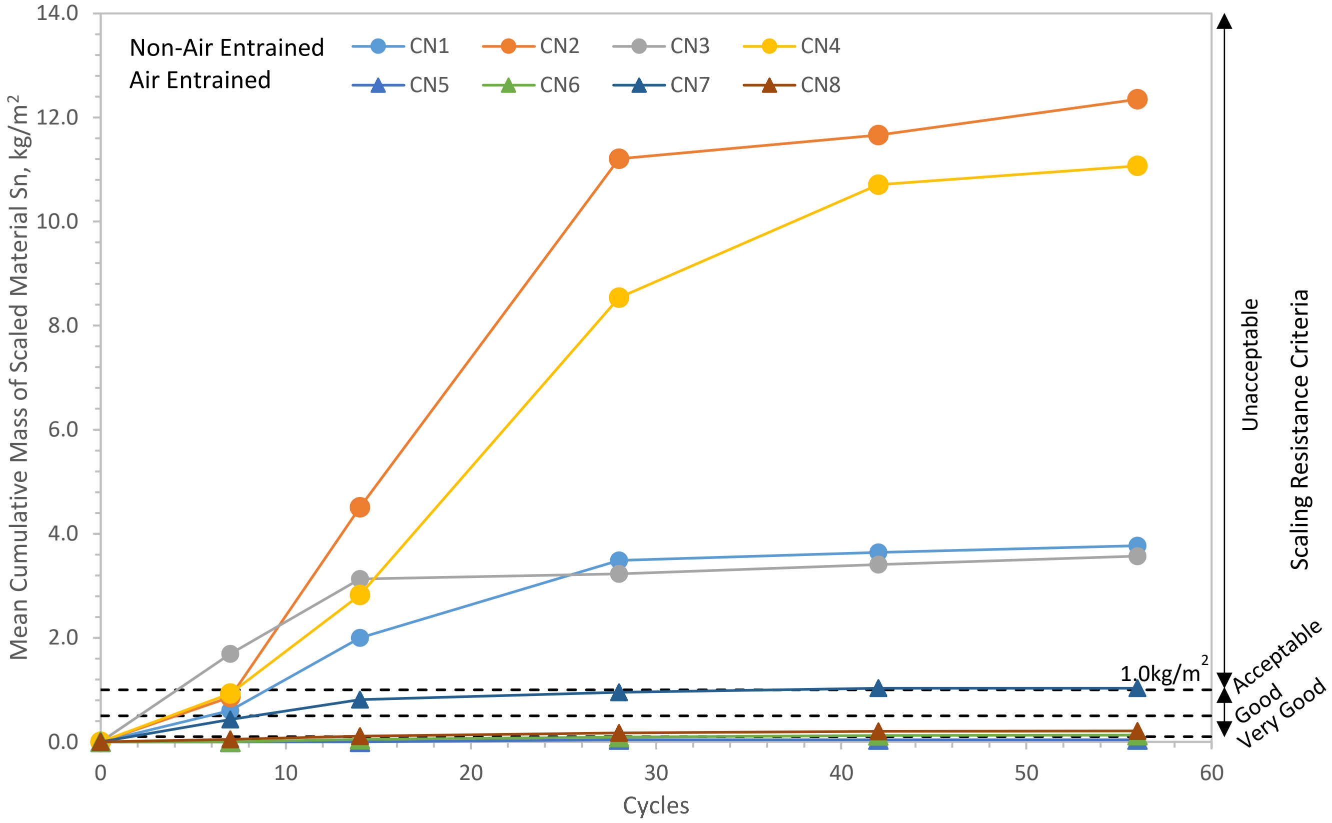


Figure 7.17 Freeze-thaw scaling results of carbonated concretes with different cement types for both air and non-air entrained samples and the scaling criteria in accordance with SS 13 72 44

Table 7.8 Scaling criteria results for different carbonated concretes showing the approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	**Mix Characteristics**			**Sn_{56}, kg/m^2**	**Approx. Cycle No. of Limit $Sn \geq 1.0$kg/m^2**	**Sn_{56}/ Sn_{28}**	**Rate of Deterioration**	**Scaling Criteria**
	Concrete Type	**w/c**	**Air Content, %**					
Non-Air Entrained								
CN1	CEM I	0.54	1.2	3.77	7 – 14	1.08	1.5831ln(x)	Unacceptable
CN2	CEM II/B-V	0.47	1.5	12.35	7 – 14	1.10	5.9313ln(x)	Unacceptable
CN3	CEM III/A	0.52	1.6	3.57	0 – 7	1.11	0.8033ln(x)	Unacceptable
CN4	CEM II/A-L	0.54	1.4	11.07	7 – 14	1.30	5.4139ln(x)	Unacceptable
Air Entrained								
CN5	CEM I	0.45	4.3	0.04	na	1.00	0.0236ln(x)	Very Good
CN6	CEM II/B-V	0.4	5.0	0.13	na	1.44	0.0633ln(x)	Good
CN7	CEM III/A	0.44	4.8	1.03	28 – 42	1.08	0.2829ln(x)	Unacceptable
CN8	CEM II/A-L	0.45	4.5	0.21	na	1.24	0.0793ln(x)	Good

Na – not applicable

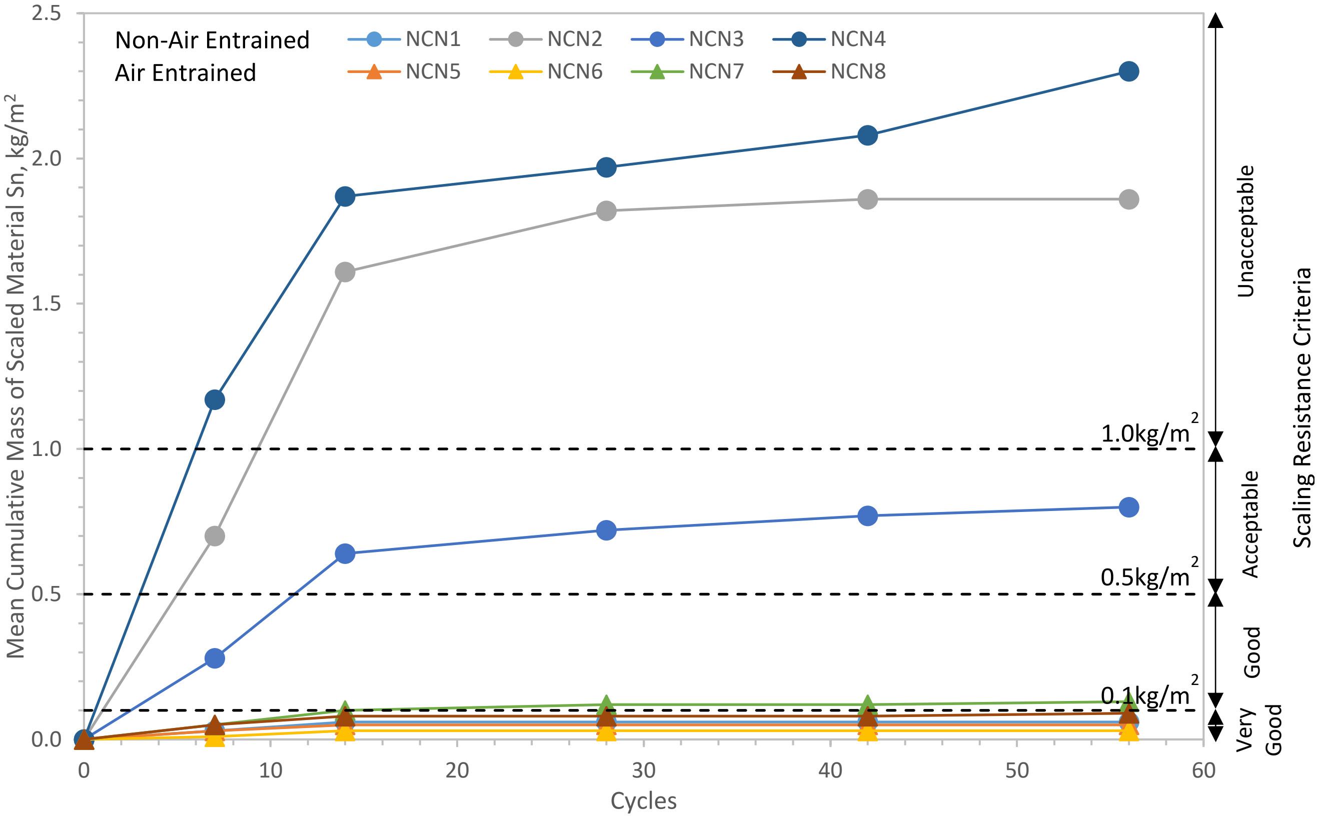


Figure 7.18 Freeze-thaw scaling results of non-carbonated concretes with different cement types for both air and non-air entrained samples and the scaling criteria in accordance with SS 13 72 44

Table 7.9 Scaling criteria results for different non-carbonated concretes showing the approximate cycle of unacceptable damage and the equation for the rate of deterioration

Mix Code	**Mix Characteristics**			**Sn_{56}, kg/m²**	**Approx. Cycle No. of Limit $Sn \geq 1.0 kg/m^2$**	**Sn_{56}/Sn_{28}**	**Rate of Deterioration**	**Scaling Criteria**
	Concrete Type	**w/c**	**Air Content, %**					
Non-Air Entrained								
NCN1	CEM I	0.54	1.1	0.06	na	1.0	0.0125ln(x)	Very Good
NCN2	CEM II/B-V	0.47	1.7	1.86	7 – 14	1.02	0.5244ln(x)	Unacceptable
NCN3	CEM III/A	0.52	1.2	0.8	na	1.11	0.2328ln(x)	Acceptable
NCN4	CEM II/A-L	0.54	1.1	2.3	0 – 7	1.17	0.4769ln(x)	Unacceptable
Air Entrained								
NCN5	CEM I	0.45	4.6	0.05	na	1.0	0.0083ln(x)	Very Good
NCN6	CEM II/B-V	0.4	4.8	0.03	na	1.0	0.0083ln(x)	Very Good
NCN7	CEM III/A	0.44	4.2	0.13	na	1.08	0.0358ln(x)	Good
NCN8	CEM II/A-L	0.45	4.0	0.09	na	1.13	0.0156ln(x)	Very Good

Na – not applicable

The topic of whether carbonation improves or hinders the strength of concrete is a large discussion area between engineers and scientists. But these discussions relate to how well the carbonated concretes react under loading. Figure 7.19 shows a comparison between carbonated and non-carbonated freeze-thaw data for the different concrete types. Considering the differences in the mass loss between the carbonated and non-carbonated samples, Figure 7.19 shows that with the inclusion of carbonation the concrete becomes weaker resulting in more scaling to occur. This suggests that the following hypothesis:

Carbonation of concrete is a hindrance to the durability of during freeze-thaw conditions for non-air entrained concrete when compared to non-carbonated. However, with the addition air entraining admixture, the AEA appears to provide further protection when the microbubbles interact with the carbonates resulting in the premise that with AEA, concrete could resist freeze-thaw conditions whether or not it was carbonated.

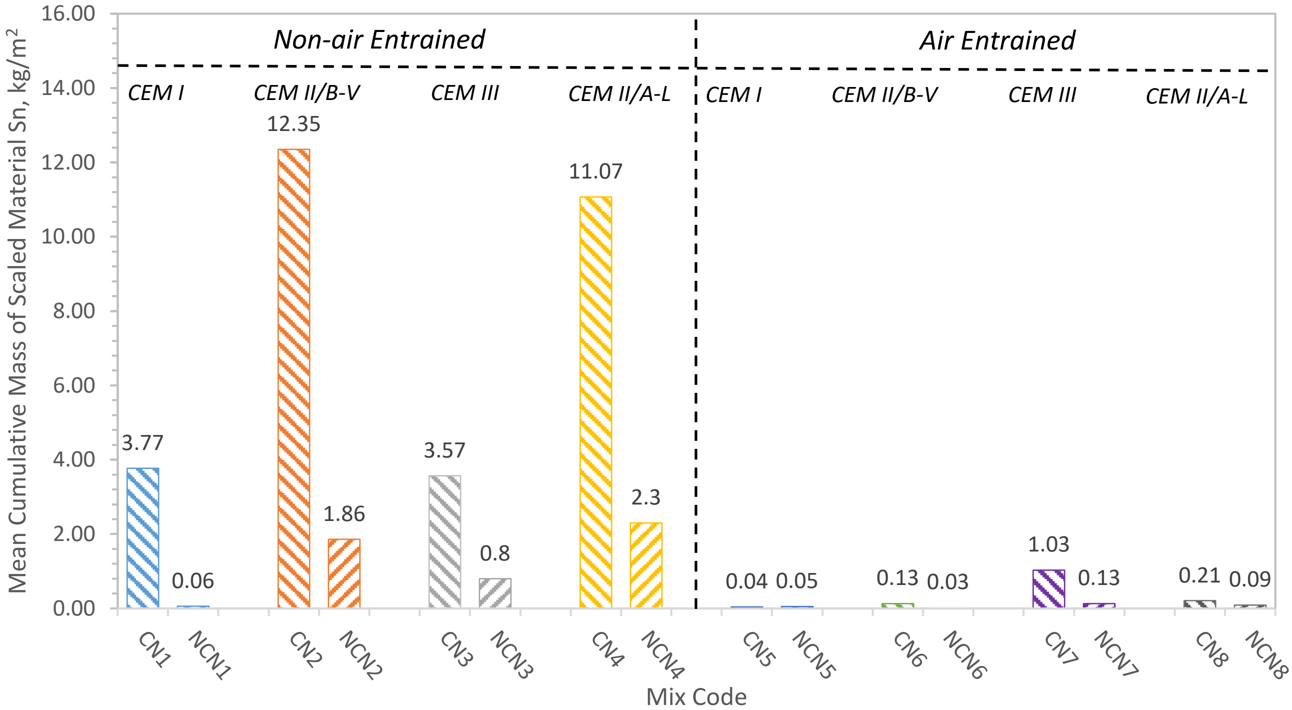


Figure 7.19 Comparison between the mean cumulative mass of scaled material (Sn_{56}) for the carbonated and non-carbonated concrete with different cement types for both air and non-air entrained with the values of the total mass loss for each concrete

Likewise, for the air entrained carbonated concretes there is a slight increase in the material loss one the concretes have been carbonated. Although the air entrained carbonated concretes had slight higher material loss than their non-carbonated counterparts, there was a large reduction in the material loss than the non-air entrained concretes suggesting that even though the air entrained concretes deteriorate still, the air entrainer in the concrete protects the concrete during the freeze-thaw testing displaying the possibility that the air entrainer that lines the wall of the entrained air voids solidifies/densifies with the concrete to provide a hardened surround to reduce cracking.

Furthermore, the increase in the material loss especially for non-air entrained carbonated samples suggests that the work conducted by Kleiger (1990) is true as the outer most layer of the concrete is the poorer layer and tends to fail easily and quickly when subjected to the external environment. Figure 7.20 shows images of carbonated concrete once it has been tested for freeze-thaw deterioration.

(a) *(b)*

Figure 7.20 CEM II/B-V non-air entrained carbonated concrete (a) before and (b) after the scaled material has been removed from the surface

7.6 Summary of Chapter 7

This chapter considered changing several parameters which influence freeze-thaw CEN test method to better represent how the UK and European climates. The modifications to the standard allowed a more accurate and realistic representation of the climate to better compare laboratory results to the results seen after freeze-thaw attack.

The influence of changing the temperature profile was a major parameter change for the test as it allowed a more realistic comparison to be with the temperatures the concretes are subjected to through the winter months. Two variations were used, changing the maximum and minimum values closer to what were seen in previous years. From the testing, it showed that Variation 1 temperature profile was still as damaging compared to the CEN test despite the maximum temperature reaching +13°C (from +23°C) and the minimum temperature being increased to -13°C (from -18°C). Variation 2 saw very little scaling of the samples even with the temperatures down at -8°C for several hours. This dictates that there is a minimum temperature whereby scaling does and does not occur meaning that concretes need only be designed for a minimum temperature which would be suitable for even the harshest of conditions.

Changing the temperature profile has shown to have detrimental effects on the concrete as shown from Variation 1 temperature profile. The NaCl concentration has also shown to have major damaging effects when tested for freeze-thaw. As the results above show, the increase in the NaCl concentration does in fact protect against scaling typically seen when NaCl solution is applied but what is more interesting is with the increase in the concentration the damage to the concrete is significantly worse the CEN test. It was observed that with different concentration levels came different levels of cracking:

- 3% saw scaling of the test surface;
- 6% saw minor surface cracks but not enough for the solution to drain away;
- 9% saw a high number of minor cracks (up to 1mm) throughout the concrete, enough to prevent the test from continuing and;
- 12% saw a small number of major cracks (measuring up to 3mm in width) throughout the concrete causing large pieces to come away so easily.

The test of the different concentrations showed that with multiple applications of de-icing salt, the concrete can quickly crack and spall of the section. This combined with the weaker surface concrete layer can potentially cause the concrete to fail sooner rather than later if continuous applications of de-icing salt.

Testing the cast surface of the concrete samples provides a basis for how well the concrete can withstand freezing and thawing in the real world. These results show that the cast surface, when exposed to freeze-thaw, can seriously impact how well the concrete performs along with the aesthetics of the concrete finish. Testing the cast surface provided insight into how well the concrete surface (namely the weaker layer of the concrete) reacts when subjected to freeze-thaw. As shown the concrete did not provide the protection required and ultimately several test samples did not reach criteria. Though a few of the samples did not perform as well, this test method gave a clearer idea on how well the concrete surface would perform. As for the air entrained samples, the showed to have similar freeze-thaw resistance as their CEN test counterparts with minimal scaling occurring.

Considering the cumulative mass of scaled material from the sides and base, there is not a requirement for this to be considered for inclusion in the standard. Although several samples were rated good before the addition which then changed the rating of the samples to acceptable the samples still achieved a suitable scaling rating. On the other hand, for samples which had already reached an unacceptable rating, were the samples that suffered from additional scaling from the sides and base. These were typically the samples which were not air entrained except for CEM III/A which scales for both air and non-air entrained.

Testing the influence of carbonation on freeze-thaw deterioration abled for realistic analysis of the concrete's performance. Ideally, the concrete would be subjected to simultaneous accelerated carbonation and accelerated freeze-thaw whilst under constant loading to fully scope the concretes durability. The procedure used provided results to determine that regarding the combination of carbonation and freeze-thaw attack, concrete performs worse once it has been carbonated. All concrete in the UK is subjected to carbonation for the simple fact that there always carbon dioxide (CO_2) in the atmosphere which infiltrates the concrete reacting with the calcium to produce calcium carbonates. Previous testing and analysis has looked at carbonation and freeze-thaw mechanisms separately which has not identified a link between the two despite the fact that concrete is subjected to both of these (and other mechanisms) at the same time. Further research into the combinations of freeze-thaw and carbonation attack but initial results indicate that it is simply not one after another affecting the durability of the concrete but rather combination of all.

Overall the various parameters which have been modified to suit the climate and the various conditions which the concrete is subjected to are a basis for updating the standard to better access a concretes durability aspects for not only the UK climate but to other European countries who has a wet and cold climate similar to the UK.

Chapter 8
Conclusions, Practical Implications and Recommendations for Further Work

8.1 Introduction

The introduction of new European sustainability agendas for decreasing the amount of CO_2 produced has forced the concrete industry to pull away from using standalone CEM I in the concrete and using cementitious by-products from other industries (fly ash from burning coal and GGBS from smelting pig iron) to reduce waste and CO_2 emissions. These agendas coupled with the European standards for concrete design, which focus more on performance-based specification, have led to the inclusion of cementitious materials for concretes subjected to aggressive environments. Furthermore, with climate change influencing the dynamic of concrete design in construction, the current testing standards for concrete do not show a true representation of a concrete's performance in these harsh environments.

The study focused on the influence of different cement types on freeze-thaw performance in the UK climate with the development of a new testing regime for freeze-thaw considering different testing parameters which more closely represent the UK and European climates. These parameters include changing the temperature envelope, varying the salt concentration and the influence of carbonation on freeze-thaw salt scaling deterioration. A selection of cement types were used as described in BS EN 197-1 using the maximum allowable replacement content for concretes which would be subjected to freeze-thaw in accordance with BS 8500. This was coupled with the microstructural analysis of the concretes to identify a correlation between the air void analysis and freeze-thaw scaling results and whether said results could pinpoint the concretes that were unable to maintain operation in these environments.

The current standard for freeze-thaw testing observes the process which the concrete reacts to the saline solution infiltrating the concrete microstructure whilst subjected to a temperature envelope that tests the concrete to extreme temperatures rarely seen in the UK. Using a selection of materials including CEM I, CEM II/B-V, CEM III/A and CEM II/A-L freeze-thaw testing was conducted using design strengths ranging from 20-60 MPa for non-air entrained and 20-50 MPa for air entrained samples. The BRE design guide (1997) was used to design the concretes and it should be observed that a 60 MPa air entrained concrete was not possible in accordance with the guidance.

Given the low repeatability and reproducibility of the freeze-thaw test and how different the results can be from samples of the same concrete batch, the microstructural properties were also analysed to determine a relationship between the internal microstructure and the freeze-thaw resistance. This study also considered the influence of different aggregates on the concrete's performance, particularly the influence of lightweight aggregate and how this material acts like air entrainment to reduce the amount of surface scaling.

The main conclusions from each phase of the research study are summarised at the end of each Chapter. This Chapter compiles the conclusions from the study and defines the practical implications from the conclusions detailed throughout. This Chapter concludes with recommendations for future work based upon the studies conducted throughout this research project.

8.2 Overall Conclusions

The aim of the project was to investigate the CEN/TS 12390-9 method and associated acceptance criteria as means of evaluating air-entrained concretes or equivalent for use in UK exposure conditions. The following objectives have been set to meet this aim and concluded with the findings from the project:

I. *Establish the range of materials for and suppliers of the test concretes for the investigation. These will include concretes containing fly ash, GGBS and limestone all with F/T resisting aggregates. Carry out F/T scaling tests following the CEN/TS 12390-9 (3.0% NaCl) method to determine the performance of the test concretes.*

Various cement types were used during this research project to understand how they would perform during freeze-thaw for both air and non-air entrained. These were designed to have a target strength comparing the various materials used in industry. A range of target strengths, air and non-air entrained, different addition contents and air contents were considered to review each of these restrictions and determine if these non-compliant samples could still be used and would achieve an *Acceptable* scaling rating.

The use of air entrainment caused the water/cement ratio to decrease compared to their non-air entrained counterparts to accomplish the target strength to consider compressive strength loss from air entrainment. Although the compressive strength does decrease with the inclusion of air entraining admixture, target strength was still reached and perform better for freeze-thaw than non-air entrained concretes.

CEM I was the cement types easiest to air entrain as minimum volumes were required coupled with the use of superplasticizer provide the required air content. CEM III/A and CEM II/A-L slightly more difficult due to the addition with CEM III/A not requiring air entrainment as it has the capability to withstand freeze-thaw salt scaling or chloride ingress naturally. Air entrainment was added to the mixes however from the results collated from the non-air entrained samples it was not required. If anything, it only increased the scaling of the material as this could have allowed better access for the saline solution to freeze causing more scaling to occur. CEM II/A-L was observed to have more scaling loss than CEM I due to the addition of limestone of 20% replacement but still achieving the required target strength. Scaling for CEM II/A-L observed to have a similar trend to CEM I where majority of the samples achieved the minimum *Acceptable* scaling rating only with slightly higher values despite having a lower CEM I content. This suggested that the particle size distribution influenced the results since the material is chemically inert. The D_{90} values for both materials show that limestone had a smaller average size compared to CEM I allowing for the particles for be packed closer together reducing the void space.

II. *Use an automatic image analysis system and follow the BS EN 480-11 and ASTM C457 measurement methods, to quantify the air void characteristics of the test concretes.*

Simply testing a range of concretes with different design strengths is not enough to determine the freeze-thaw resistance of a concrete, a more detailed analysis was required to understand the internal microstructural layout of a sample. Previous studies had confirmed a concrete had the capacity to reduce freeze-thaw if the spacing between the voids was less than 250μm. This is known as the Powers Spacing Factor. However, continual development of cement types and admixtures had made the air void parameter less reliable due to the nature of new admixtures and their secondary benefits particularly in third generation superplasticizers with poly carboxyl activator. As with previous studies (Hasholt, 2014), this research project had identified that the Spacing Factor, whilst still used a guideline, is difficult to use in conjunction with other parameters to determine freeze-thaw resistance as each parameter would produce results contradicting one another .

Instead of using the Spacing factor to determine a concretes freeze-thaw resistance, it had been determined that using the void frequency would produce a better approximation combined with the microair content detailed in BS EN 480-11. The microair content detailed in the standards is not a good measure in its current definition. It does not fully represent the number of voids which provide freeze-thaw protection. Microair content, defined in BS EN 480-11, is the total air content of all the voids below 300μm in diameter which tends to equate to approximately 75-80% of the total air content of a sample. The issue with using this parameter is that most of the voids counted are within the 0-30μm size range which influence the air content and the spacing factor. Approximately 68% of the total number of voids counted accounts for the number of voids counted in the 0-30μm range meaning that there is a large percentage of voids that are negligible in regards to being able to fill with water as they are too small, hence not able to contribute to the freeze-thaw resistance. Whilst the void count is high the total air content for this size range calculates to be 0.62% of the total air content which is not much compared to the overall air content. Therefore, it should be considered that changing the range of the microair content to start from 30μm to 300μm would be more suitable otherwise the microair content parameter should not be included with the calculation altogether.

III. *Analyse the recommended concretes for XF4 Exposure Class to determine how resistant these concretes are to freeze-thaw, in particular to concretes containing lightweight aggregate and compare to other XF resisting aggregates.*

During research, it was confirmed that the aggregates influence the freeze-thaw resistance of a concrete. BS 8500 details that for concrete to be subjected to XF3/XF4 there is a requirement for freeze-thaw resisting aggregates. Granite and gravel aggregates were compared to investigate their influence in freeze-thaw resistance/deterioration and how they influence the microstructural characteristics of the air voids . Granite showed to have very good resisting properties reducing the mass of scaled material, which decreased further when the concrete was air entrained.

Using gravel provided different results as it became easier for the saline solution to infiltrate the aggregate and since gravel used on this project is not a freeze-thaw resisting material in accordance with BS EN 1367-1 there was more scaled mass loss as the aggregate deteriorated during freeze-thaw. From this it can be concluded that the choice of aggregate significantly affects the freeze-thaw resistance.

From the analysis conducted the results show that using lightweight aggregates in a concrete provides a resistance freeze-thaw attack. The scaling results illustrate that the concrete has an air content (which varies depending on the aggregate quantity) able to provide protection. However, when tested using the magnesium sulphate (MS) test method, the results showed that the aggregate had an MS value of 38 stating the aggregate would not be suitable to withstand freeze-thaw. However, testing showed negligible mass of scaled material was measured providing similar results to concretes with air entrainment. This suggests that with-it high-water absorption value, lightweight aggregate absorbs the saline solution before freezing and due to the high porosity of the aggregate, can stop freeze-thaw damage. Furthermore, once the solution has evaporated into the atmosphere, it can be assumed that, the salt crystals which are left behind build up over time increasing the salt concentration within the voids of the material preventing further frost build up. It can be concluded that if a concrete was to be subjected to freeze-thaw attack and no air entrainment was to be used then lightweight aggregate would be the choice of material due to the high volume of natural voids within the aggregate acting as air entrainment.

From the compressive strength results, it was noted that despite a non-air entrained concrete having a higher strength it did not have the capacity to withstand freeze-thaw attack the same way that air entrainment did. There was a notable trend in the results showing that a similar distribution of results could be seen between air and non-air entrained concretes however the freeze-thaw scaling results were higher for non-air entrained. That being said, many of the non-air entrained concretes were able to achieve an *Acceptable* rating in accordance with SS 137244 and whilst it is in the opinion of the author that air entrained concretes should always be used in a freeze-thaw environment, there is still the option for a higher strength non-air entrained concrete to be used. Though this approach should only be used when an XF2 or less exposure class is the base of the design.

IV. *Analyse the data from the study to examine various issues about estimating F/T damage (from fresh air content/air void characteristics), rates of deterioration within and between concretes, and comparisons between laboratory and field behaviour.*

Analysis of the fresh air content led to the conclusion that if a concrete was air entrained then it would be capable of resisting freeze-thaw attack as described in Table A.9 of BS 8500. However, it was concluded from the data that simply air entraining a concrete did not provide an *Acceptable* scaling rating nor did a higher strength. These were dependent on the cement type used coupled with the water/cement ratio and concretes that were air entrained but had a 20-30 MPa strength did not achieve an *Acceptable* rating nor did a 50 MPa non-air entrained CEM II/B-V concrete.

The data analysed in this study led to the possibility of deriving an equation which could be implemented based on the data collated from the 56-cycle freeze-thaw testing regime similar to that for carbonation and chloride ingress. A rate of deterioration equation was developed based upon the data collected over the 56 cycles that would allow for a logarithmic 'best fit' line producing an equation which can then be used to determine the mass loss at a particular cycle or when the scaling loss is negligible. The freeze-thaw scaling data will produce a graph showing the cumulative mass of scaled material over the testing period showing the graph is consistently increasing as there was constant scaling. This developed the equation for deterioration:

$$y = m\ln(x)$$

Comparison were undertaken between laboratory and industry produced concretes to understand the relationship of industry relative to the standards. It was identified that all the concretes were in accordance with BS 8500 but more importantly they ensured it would achieve the minimal scaling loss during the test.

V. *Identify suitable test conditions/performance criteria for modifying the CEN/TS 12390-9 method, including the effect of carbonation, varying salt concentration and temperature profile representing real time deterioration to achieve a particular mass loss, as appropriate.*

The changing climate has seen milder winters increasing whilst the harsh winters are becoming less frequent. This means that the current CEN/TS 12390-9 is considered to be too harsh relative to the winters that the UK is currently experiencing. A series of concretes were tested with various parameters modified to better represent the freeze-thaw conditions seen and more likely to be experienced in the future. The resulting data showed that the concrete subjected to different temperature envelopes scaled differently not just because of the temperature change but also due to the duration it was held at. With a temperature envelope less severe than the CEN profile, the new envelops became narrower in the sense that the temperature did not have a larger change to go through meaning the freezing temperatures could be held for longer allowing more water in the voids to freeze increasing the amount of mass loss.

The inclusion of carbonation into the freeze-thaw test method tried to mimic the deterioration seen throughout the year when concrete elements are continuously subjected to carbon dioxide. This combined with freeze-thaw must causes significant deterioration for the concrete especially for those which were not air entrained. Observations indicated that the air entrained concretes shown minimal scaling once carbonated making them stronger and more resistant to freeze-thaw signifying that with the removal of the carbonates, causes the thin air entrainer film of the air void to solidify increasing its resistance. Whereas with non-air entrained the concrete deteriorates rapidly leading to major cracking throughout the sample.

8.3 Practical Implications

The Exposure Classes defined in BS EN 206-1 and BS 8500 outline the specifications for a concrete's performance, in particular, the designation for XF. Although these are clearly defined, they do not detail the exposure seen in the UK, particularly when the salt concentration increases due to constant applications. This has led to the derivation of an XF5 Exposure Class.

Through the course of this research project, concretes have been designed with a designed target strength for both air and non-air entrained concretes ensuring that the replacement contents (BS 8500 compliant concretes, Series 1 and 2 design mixes) do not exceed the standard guidelines for replacement contents relative to freeze-thaw in order for base line results to be determined. However, for the rare occasion where a concrete would be subjected to extreme temperatures an additional class should be included for instances where concrete would be subjected to permanent saturation and prolonged continuous saline applications. For this, the addition of XF5 would provide guidance on continuous applications of de-icing salt or sea water:

Class XF5 – Permanent saturation with prolonged continuous applications of de-icing salt or sea water

During this this research project concretes have been tested to the CEN/TS 12390-9 test method for freeze-thaw resistance whereby the exposure classes for freeze-thaw have been divided into four classes to simulate different environmental conditions. Though these classes detail individual exposure conditions which the concrete could be subjected they do not fully explain the damage seen in concrete in recent years.

Unlike XF4 where there is high saturation and (it is assumed) one application of de-icing salt or sea water, XF5 describes situations where the concrete is close to being completely water saturated, is continually subjected to multiple layers of de-icing salt or sea water and constant temperature cycling which drops below freezing and thawing. Examples of this would be motorways and bridges which are used every day which require continual applications of de-icing salt to prevent ice build-up. Sea walls and piers has the tide continually moving in and out, similar to bridge decks, has numerous applications of salt water. Considering an additional class (XF5) would be implemented into the design codes for concrete that would be subjected to continual salt/de-icing salt applications with average coverage rate approximately 178 – 268 g/m^2. The definition of XF5 is described as:

XF5 class would assume that the concrete would have permanent saturation with continuous prolonged applications of salt whilst subjected to constant wetting and drying cycles.

Table 5.13 shows the exposure classes seen in BS 8500 and BS EN 206 describing the typical situations for each class and an additional class for XF5. With the addition of another XF Exposure Class, further details on defining the minimum cement and air contents are shown in Table 5.14.

The microstructural characteristics of the concrete influenced the resistance of freeze-thaw namely the size and distribution of the voids. As a first verification for determining a concrete's performance, the void frequency (number of voids over the traverse length) is shown to be a good approximation to determine a concrete's performance. The results showed that if the void frequency was between then it would have the resisting properties required to reduce freeze-thaw attack.

Development of simulated models for carbonation and chloride ingress led to the derivations of equations which could detail approximately the life span of a concrete subjected to certain environments. During this research a similar equation has been derived for freeze-thaw aptly named Freeze-Thaw Rate of Deterioration whereby the results of the tested concretes were used to create a logarithmic function to determine the mass of material lost per m^2 per cycle. Whilst further research and derivation is required this part of the equation outlines a rate for a specific concrete determining future material loss for a particular cycle.

The performance of concrete in freeze-thaw conditions can be greatly improved by changing the type of aggregate from normal/freeze-thaw resistant to lightweight. As shown in Chapter 6, lightweight has the capacity to act like air entrainment whilst still being a bulk material. The physical attributes of the material including the pore size distribution replicate that of a standard air entrained concrete with other benefits including a reduction in quarrying and transporting the aggregate and an economical benefit of not requiring large amounts of air entraining admixture.

8.4 Recommendations for Future Research

From the conclusions and the practical implications already discussed, several possible areas for future research could be investigated. The following areas have been considered for study during this research and whilst the author of this thesis did not have the time to research them, it is suggested that they could be used for future works:

I. Several binary concretes were tested during this research project to understand how replacement materials resist freezing and thawing. A further study into how tertiary mixes would influence a concrete's ability against attack and the microstructural properties of the combined materials. Included should be various mixes of CEM I, fly ash, GGBS and limestone as each has their own properties that could potentially increase a concrete's resistance.

II. Combining freeze-thaw and chloride ingress and carbonation. A described in this research project, it is not simply one deterioration attack that causes concrete to fail but rather a combination of different attacks depending on the environment. This research looked at the concrete's durability once it was freeze-thaw tested after it had been subjected to carbonation. Similarly, concrete could be subjected to both chloride ingress and carbonation before being subjected to freeze-thaw which would replicate the ingress of chlorides during the rest of the year.

III. Further develop the modifications done on the existing CEN/TS 12390-9 test method. A series of modifications have been tested in Chapter 7 as to whether the freeze-thaw test method could be changed to better suit the country's climate. The data has shown that there is room to add or change parameters for the test method to test the concrete more specific to a country's climate and environmental factors such as the amount of salt applied to a road during the winter months. Mainly, the temperature profile could be narrowed down to find the optimum temperature profile to ensure that both a milder and harsh winter are tested fully.

IV. Combine the analysis from the micro-CT scanner and the air void analyser. Currently the CT scanner can produce a 3D image and determine the porosity of a sample, however there is a possibility that the CT imagery could be combined with the computational analysis software from the air void analyser that would have the capability to determine the air void characteristic for a 3D image rather than the current 2D image.

V. Development of the rate of deterioration to create an equation for the freeze-thaw deterioration mechanism. This study derived an initial rate of deterioration equation based upon the 56 cycles of the freeze-thaw test which could then be used to determine the mass of scaled material at any cycle. Based on this, an equation should be developed to incorporate external and environmental factors as with the carbonation and chloride ingress equations to achieve a more accurate value for deterioration rate.

VI. Further investigate the influence of carbonation on the densification of air entrained concretes. Non-air entrained concretes were observed to underperform after carbonation than non-carbonated concretes which is a contradiction of previous studies. A study should be conducted to determine why the densification does improve the performance of non-air entrained concretes compared to the air entrained counterparts.

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Appendix 1
Data Sheets for Admixtures

MASTER®
» BUILDERS
SOLUTIONS

MasterAir 130

Air entraining admixture for mortar & concrete – BS EN 934-3: T2 & BS EN 934-2: T5

DESCRIPTION

MasterAir 130 is a liquid air-entraining admixture which produces ultra-stable air bubbles with good bubble size and spacing factor. It is particularly suitable for use in both mortar and concrete applications.

FIELDS OF APPLICATION

Entraining controlled air contents in a wide range of mortar and concrete types:

- Ready-to-use retarded mortar
- Air entrained concrete
- Machine and hand laid pavement quality concrete
- Low slump concrete
- Concrete containing pulverised fly ash (PFA)
- Concrete containing large amounts of fine materials

FEATURES AND BENEFITS

MasterAir 130 is especially beneficial in the production of retarded ready-to-use mortar; its formulation has been optimised to maintain air contents for up to 72 hours, when used in conjunction with retarders from our range such as MasterSet R 510. MasterAir 130 is especially useful in the types of concrete known for their difficulty to entrain and maintain the desired air content.

Entrainment of the optimum air content in mortar and concrete results in the following improvements to quality:

- Increases open time of mortar
- Improves cohesiveness and bond strength
- Increased freeze/thaw damage resistance
- Improves finish after pointing.
- Reduced permeability
- Reduced segregation and bleeding
- Improved plasticity and workability
- Increased resistance to scaling

DOSAGE

There is no standard dosage rate for MasterAir 130 admixture. Trial mixes should determine the exact quantity of air-entraining admixture. Factors to consider are: temperature, cement content and type, sand grading, sand-aggregate ratio, slump, means of conveying and placement, use of extra fine materials such as fly ash and microsilica.

The amount of MasterAir 130 admixture used will depend upon the amount of entrained air required under actual job conditions. In an initial trial mix, we suggest using 350 ml per 100 kg of cement and adjust in the light of results obtained

COMPATIBILITY

MasterAir 130 can be used with most types of EN 197 Cements. For use with Pulverised Fuel Ash, or any other special cements, contact our Technical Services Department.

MasterAir 130 should not be pre-mixed with other admixtures. If other admixtures are to be used in concrete containing MasterAir 130 they must be dispensed separately.

MasterAir 130 is compatible with mortar and concrete containing other MBCC admixtures or admixture systems – water reducers, high-range water reducers, accelerators, retarders and water repellents. For retarded mortar, it is particularly effective when used in combination with MasterSet R 510.

When such complimentary admixtures are required it is important that laboratory trials are performed, prior to any supply, to determine the respective dosages of any complimentary admixture, and the suitability, in the fresh and hardened state, of the resultant mortar or concrete. In these circumstances we recommend that you consult our Technical Services Department for further advice.

PACKAGING

MasterAir 130 is supplied in 1000-litre IBC's and 15-litre containers.

CONTACT DETAILS

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www.master-builders-solutions.com/en-gb

MasterAir 130

Air entraining admixture for mortar & concrete – BS EN 934-3: T2 & BS EN 934-2: T5

Product Data - General	
Appearance:	Yellow Liquid
Specific gravity @ 20°C:	1.01 ± 0.02 g/cm³
pH-value:	10 ± 1
Alkali content (%):	≤ 1.0% by mass
Chloride content (%):	≤ 0.10% by mass
Solids content:	7.0 ± 0.7%
Corrosion behaviour:	Contains only components according to BS EN 934-1:2008, Annex A.1
Dangerous substances:	No Performance Determined
Durability:	No Performance Determined
Product Data - BS EN 934-3: T2 - Mortar	
Air Content after standard mixing:	17.0% ± 3%
Air Content after 1 h standing:	Reference mix, minus a maximum of 3%
Air Content after extended mixing:	Air content at standard mixing ± 5%
Reduction in water requirement for standard consistence:	≥ 8% by mass
Compressive strength - 28 days:	≥ 70% of Reference mix
Product Data - BS EN 934-2: T5 - Concrete	
Compressive strength – 28 day:	≥ 75% of Reference mix
Air content in fresh concrete:	≥ 2.5% by volume of Reference mix and total air content between 4% and 6%
Air void characteristics in hardened concrete:	Spacing factor in test mix ≤ 0.200 mm
Logistics	
Shelf life:	12 months if stored according to manufacturer's instructions in unopened container.
Storage conditions:	Store in original sealed containers and at temperatures between 5°C and 30°C. Store under cover, out of direct sunlight and protect from extremes of temperature. Failure to comply with the recommended storage conditions may result in premature deterioration of the product or packaging.
Handling and transportation:	Refer to MasterAir 130 Safety Data Sheet
Disposal:	Refer to MasterAir 130 Safety Data Sheet

MasterAir 130

Air entraining admixture for mortar & concrete – BS EN 934-3: T2 & BS EN 934-2: T5

Health and Safety
"For full information on Health and Safety matters regarding this product the relevant Health and Safety Data Sheet should be consulted.

The following general comments apply to all products.

As with all chemical products, care should be taken during use and storage to avoid contact with eyes, mouth, skin and foodstuffs, (which may also be tainted with vapour until the product is fully cured and dried). Treat splashes to eyes and skin immediately. If accidentally ingested, seek medical attention. Keep away from children and animals. Reseal containers after use.

Spillage
Chemical products can cause damage; clean spillage immediately.

DISCLAIMER
"Master Builders Solutions UK Ltd" (the Company) endeavours to ensure that advice and information given in Product Data Sheets, Method Statements and Material Safety Data Sheets (all known as Product Literature) is accurate and correct. However, the Company has no control over the selection of its products for particular applications. It is important that any prospective customer, user or specifier, satisfies him/her-self that the product is suitable for the specific application. In this process, due regard should be taken of the nature and composition of the background/base and the ambient conditions both at the time of laying/applying/installing the material and when the completed work is to be brought into use.

Accordingly, no liability will be accepted by the Company for the selection, by others, of a product, which is inappropriate to a particular application.

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BUILDING TRUST

PRODUCT DATA SHEET
Sika® Aer-46

AIR ENTRAINING CONCRETE ADMIXTURE

PRODUCT DESCRIPTION

Sika® Aer-46 is a liquid air entraining concrete admixture which is formulated from modified naturally occurring and synthetic surfactants. It meets the requirements of BS EN 934-2.

USES

- Sika® Aer-46 promotes the distribution of microscopic air bubbles throughout the cement matrix.
- Applications that require high resistance to freeze/thawing cycles
- Concrete that will be exposed to tidal conditions, splash zones and de icing salts

CHARACTERISTICS / ADVANTAGES

- Provides consistent bubble size and spacing
- Improved cohesion
- Improved workability
- Improved rheology
- Reduced permeability
- Reduced bleeding
- Reduced laitance, enhancing the concrete's resistance to frost attack
- Reduced loss of air from fresh concrete

APPROVALS / STANDARDS

Conforms to the requirements of BS EN 934-2 Table 5 DoP 02 14 03 02 100 0 000085 1088, certified by Factory Production Control Body 0086, Certificate 541325, and provided with the CE mark

PRODUCT INFORMATION

Chemical Base	Modified surfactants
Packaging	20 litre drum, 200 litre drum, 1000 litre IBC
Appearance / Colour	Clear Liquid
Shelf Life	12 months from date of production if stored properly in undamaged containers.
Storage Conditions	Store in dry conditions at temperatures between +5°C and +25°C. Protect from direct sunlight and frost.
Density	1.00 kg/l (at +20°C)
pH-Value	6.0 ± 1.0
Total Chloride Ion Content	<0.10% w/w (chloride free)
Specific Advice	Freezing Point : +1°C Effect of Overdosing : Increased air content leading to reduced densities and strength Alkali Content : <0.10% w/w
Effect on Setting	Negligible

APPLICATION INFORMATION

Recommended Dosage	0.1 -0.8% by weight of cement
Compatibility	**Sika® Admixtures:** ▪ Compatibility information available on request **Cements:** ▪ All cement combinations ▪ Pulverised Fuel Ash (PFA) is a waste product of modern electricity generation. Only use PFA complying with the relevant British Standard in structural concrete. Such material will vary within the parameters laid down in the standard. Eg fineness, carbon content and loss on ignition. As a result, the amount of Sika® Aer-46 required may vary to maintain a specific air content.
Dispensing	Sika® Aer-46 should be dispensed through suitable calibrated dosing equipment.

APPLICATION INSTRUCTIONS

APPLICATION METHOD / TOOLS

- The standard rules of good concreting practice, concerning production as well as placing, are to be followed. Refer to relevant standards. Fresh concrete must be cured properly.
- Sika® Aer-46 should not be added to dry cement
- Sika® Aer-46 should be added with the mixing water

NOTES ON APPLICATION / LIMITATIONS

- When using Sika® Aer-46 a suitable mix design is required and local material sources should be evaluated.
- Due to the significant number of constituent, mix design, manufacture and placing related factors outside Sika's control, bubble spacing determination should be carried out by the concrete producer to ensure compliance with BS – EN 934-2. Bubble spacing should be completed using the specific concrete constituents/admixture combinations. For further information see CAA Admixture information sheet AIS 16 which is available at www.admixtures.org.uk
- Support from our Technical Department is recommended

VALUE BASE

All technical data stated in this Product Data Sheet are based on laboratory tests. Actual measured data may vary due to circumstances beyond our control.

LOCAL RESTRICTIONS

Please note that as a result of specific local regulations the performance of this product may vary from country to country. Please consult the local Product Data Sheet for the exact description of the application fields.

ECOLOGY, HEALTH AND SAFETY

For information and advice on the safe handling, storage and disposal of chemical products, users shall refer to the most recent Safety Data Sheet (SDS) containing physical, ecological, toxicological and other safety-related data.

LEGAL NOTES

The information, and, in particular, the recommendations relating to the application and end-use of Sika products, are given in good faith based on Sika's current knowledge and experience of the products when properly stored, handled and applied under normal conditions in accordance with Sika's recommendations. In practice, the differences in materials, substrates and actual site conditions are such that no warranty in respect of merchantability or of fitness for a particular purpose, nor any liability arising out of any legal relationship whatsoever, can be inferred either from this information, or from any written recommendations, or from any other advice offered. The user of the product must test the product's suitability for the intended application and purpose. Sika reserves the right to change the properties of its products. The proprietary rights of third parties must be observed. All orders are accepted subject to our current terms of sale and delivery. Users must always refer to the most recent issue of the local Product Data Sheet for the product concerned, copies of which will be supplied on request.

BASF
We create chemistry

MasterGlenium SKY 569

High range water reducing admixture for concrete - EN 934-2: T3.1 & T3.2

DESCRIPTION

MasterGlenium SKY 569 is an innovative third-generation superplasticizer based on polycarboxylic ether (PCE) polymers. It is derived directly from the Total Performance Control™ concept. MasterGlenium SKY 569 is specially engineered for ready-mix concrete. Its particular configuration allows its delayed adsorption onto the cement particles and disperses them efficiently. As compared with other PCE superplasticizers, it is possible to obtain a high quality concrete mix with accelerated strength development and extended workability without delayed setting characteristics.

TOTAL PERFORMANCE CONTROL

The Total Performance Control™ concept ensures that ready-mix producers, contractors and engineers get a concrete that is of the same high quality as originally specified; starting from production at the batching plant, to the delivery and application into place, and followed by its hardening process. Utilizing Rheodynamic™ concrete technology it provides a concrete mix with exceptional placing characteristics and accelerated cement hydration for early strength development and high-quality concrete.

FIELDS OF APPLICATION

MasterGlenium SKY 569 is used for the production of high quality ready-mix concrete particularly when high water reductions are required to overcome lower performing cementitous combinations or high water demand materials are used. MasterGlenium 569 may also be used in combination with MasterMatrix admixtures for producing:

- SDC (Smart Dynamic Concrete)
- SCC (Self-compacting concrete)

FEATURES AND BENEFITS

MasterGlenium SKY 569 offers the following benefits for:

The ready-mix producer:

- Capability of delivering high quality concrete at any time to the job site in place.
- Production of a concrete with low water cement ratio that meets EN 206-1 without loss of workability.
- Single product for many application needs.

The contractor / applicator:

- Easier placing and faster strength development.
- Improved concrete surfaces.
- Guarantee to place the same concrete as specified and ordered from ready-mix plant.
- More versatile and forgiving concrete mix.

The engineer:

- Insurance that concrete meets original specification
- High quality concrete with better durability.

DOSAGE

MasterGlenium SKY 569 is particularly suited for mixes where higher strengths/water reductions are required e.g. lower performing cementitous combinations or in high water demand material combinations are used. Compared to other products in the MasterGlenium SKY range the dosage rate may be reduced by 10 to 15% to achieve the same levels of performance.

The normally recommended dosage rate of MasterGlenium SKY 569 is approximately:

- *By Volume* - 0.19 to 1.11 litres per 100 kg of cement (binder) content.
- *By Weight* - 0.20 to 1.20 kg per 100 kg of cement (binder) content.

The dosage rates given above are for typical usages, they are not meant as absolute limits, as other dosages may be utilised in special cases according to specific job conditions. If required consult BASF Construction Chemicals Technical Services Department for advice. Trial mixes should be carried out to ensure optimum dosage and effect. Where the concrete is to be machine finished by utilising power float or power trowelling methods, we recommend that you contact the Technical Services Department for dosage rate guidance.

Date of Issue: January 2016
Version No. 4

MASTER® BUILDERS SOLUTIONS

We create chemistry

MasterGlenium SKY 569

High range water reducing admixture for concrete - EN 934-2: T3.1 & T3.2

MIXING

MasterGlenium SKY 569 is a ready-to-use admixture to be added to the concrete as a separate component. Optimal performance is obtained if MasterGlenium SKY 569 is dispensed into the concrete mix right after the addition of the first 80% of the mixing water, i.e. when all solids are wetted out. Avoid adding the admixture to the dry aggregates and cement.

COMPATIBILITY

MasterGlenium SKY 569 is not compatible with MasterRheobuild superplasticizers.

MasterGlenium SKY 569 can be used with all types of EN 197 Cements. For use with other special cements, contact our Technical Services Department.

MasterGlenium SKY 569 should not be pre-mixed with other admixtures. If other admixtures are to be used in concrete containing MasterGlenium SKY 569 they must be dispensed separately.

In order to optimize special requirements the use of the following complementary additives is suggested:

- Viscosity modifying agent MasterMatrix to produce Smart Dynamic concrete and Rheodynamic™ concrete.
- Air entraining agent MasterAir to improve frost/thaw resistance.

When such complimentary admixtures are required it is important that laboratory trials are performed, prior to any supply, to determine the respective dosages of any complimentary admixture, and the suitability, in the fresh and hardened state, of the resultant concrete. In these circumstances we recommend that you consult our Technical Services Department for further advice.

PACKAGING

MasterGlenium SKY 569 is supplied in Bulk, 1000-litre IBC's and 25-litre containers.

CONTACT DETAILS

BASF plc,
Construction Chemicals,
P.O. Box 4,
Earl Road,
Cheadle,
Cheshire, SK8 6QG
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Fax +44 (0) 161 488 5220
www.master-builders-solutions.basf.co.uk

Date of Issue: January 2016
Version No. 4

BASF
We create chemistry

MasterGlenium SKY 569

High range water reducing admixture for concrete - EN 934-2: T3.1 & T3.2

Product Data	
Appearance:	Light brown liquid
Specific gravity @ 20°C:	1.08 ± 0.02 g/cm³
pH-value:	6.0 ± 1
Alkali content (%):	≤ 2.00 by mass
Chloride content (%):	≤ 0.10 by mass
Corrosion behaviour:	Contains only components according to BS EN 934-1:2008, Annex A.1
Air Content:	Fulfilled
Water reduction:	≥ 112% of Reference mix
Increase in consistence:	Increase of ≥ 120mm from initial slump or ≥ 160mm from initial flow
Retention of consistence:	At 30 mins ≥ Reference mix at initial
Compressive strength:	Fulfilled
Durability:	NPD
Dangerous substances:	NPD
Logistics	
Shelf life:	12 months if stored according to manufacturer's instructions in unopened container.
Storage conditions:	Store in original sealed containers and at temperatures between 5°C and 30°C. Store under cover, out of direct sunlight and protect from extremes of temperature. Failure to comply with the recommended storage conditions may result in premature deterioration of the product or packaging.
Handling and transportation:	Refer to MasterGlenium SKY 569 Safety Data Sheet
Disposal:	Refer to MasterGlenium SKY 569 Safety Data Sheet

CE

Certificate No. 0086-CPD-469071
EN 934-2: T3.1 & T3.2
Declaration of Performance can be found at www.master-builders-solutions.basf.co.uk

We create chemistry

MasterGlenium SKY 569

High range water reducing admixture for concrete - EN 934-2: T3.1 & T3.2

MasterGlenium SKY 569, BASF plc, Construction Chemicals, Version 4

Health and Safety
"For full information on Health and Safety matters regarding this product the relevant Health and Safety Data Sheet should be consulted.

The following general comments apply to all products.

As with all chemical products, care should be taken during use and storage to avoid contact with eyes, mouth, skin and foodstuffs, (which may also be tainted with vapour until the product is fully cured and dried). Treat splashes to eyes and skin immediately. If accidentally ingested, seek medical attention. Keep away from children and animals. Reseal containers after use.

Spillage
Chemical products can cause damage; clean spillage immediately.

DISCLAIMER
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Number: UK9-57

DECLARATION OF PERFORMANCE

In accordance with Annex III of Registration (EU) No. 305/2011
(Construction Product Regulation)
amended by Commission Delegated Regulation (EU) No 574/2014

1 Unique identification code of the product-type:

AURACAST 200, 1009200, 1009206

2 Intended use as foreseen by the manufacturer of the construction product in accordance with the harmonised technical specification:

Admixtures for concrete, mortar and grout

3 Name, registered trade name or registered trade mark and contact address of the manufacturer as set out in article 11 (5)

Fosroc Limited
Drayton Manor Business Park
Coleshill Road, Tamworth
Staffordshire, B78 3XN, UK

4 Name and contact address of the authorised representative who has received a mandate for the tasks set out on Article 12 (2):

Not Relevant

5 System or systems for assessment and verification of constancy of performance of the construction product in accordance with Annex V

System 2+

6a In the case of a declaration of performance concerning a construction product that is covered by a harmonised standard

EN 934-2:2009 Table 3.1, Table 3.2

The notified body

BSI 0086

6b In case of a declaration of performance concerning a construction product for which a European Technical Assessment was issued

Not Relevant

Issue Number: 1

Number: UK9-57

7 Declared performance

Essential Characteristics	Performance	Harmonised technical specification
Chloride ion content	≤0.1% by mass	EN 934-2:2009
Alkali content	≤ 1.0% by mass	EN 934-2:2009
Corrosion Behaviour	Contains only components according to EN 934-1:2008 Annex A.1	EN 934-2:2009
Water reduction	Test mix ≥ 12% compared with control mix	EN 934-2:2009
Increase in consistence	Increase in slump ≥ 120 mm from initial (30±10 mm) Increase in flow ≥ 160 mm from initial (350±20 mm)	EN 934-2: 2009
Retention of consistence	In 30 min after the addition, test mix value ≥ initial value of control mix	EN934-2:2009
Compressive strength - equal consistance	At 1 day, test mix ≥ 140% of control mix At 28 days, test mix ≥ 115% of control mix	EN 934-2:2009
Compressive strength - equal W/C ratio	At 28 days, test mix ≥ 90% of control mix	EN 934-2:2009
Air Content	Test mix ≤ 2 % by volume above control mix	EN934-2:2009
Dangerous substances	NPD	EN 934-2:2009

8 Appropriate Technical Documentation and/or Specific Technical Documentation:

Not Relevant

The performance of the product identified above is in conformity with the set of declared performance/s. This declaration of performance is issued in accordance with Regulation (EU) No 305/2011, under the sole responsibility of the manufacturer identified above.

Signed for the manufacturer and in the name of the manufacturer by:

Alan Clayton

Technical Quality Manager

Alan Clayton

Place and Date of Issue: 01/02/2019 Tamworth

MasterMatrix SDC 150

High performance viscosity modifying agent (VMA) for fluid concrete - EN 934-2: T13

DESCRIPTION

MasterMatrix SDC 150 is an aqueous solution of a high-molecular weight innovative synthetic copolymer.

Thanks to its tailored mode of action in concrete, MasterMatrix SDC 150imparts a level of viscosity within a mix enabling the right balance between fluidity, passing ability and resistance to segregation to be achieved. The balance is lacking when the fluidity of the concrete is obtained by adding water.

SMART DYNAMIC CONSTRUCTION

MasterMatrix SDC 150 is a key component to our Smart Dynamic Construction concept for benefits in:

- Economy: Savings on fines (<0.125 mm), up to 40% faster placing and up to 5 times higher placing productivity
- Ecology: Less fines - less CO_2, and higher concrete durability
- Ergonomic: No vibration, no noise, low stickiness of the concrete mixture

FIELDS OF APPLICATION

MasterMatrix SDC 150 is optimized for use whenever an increase in mix viscosity would be advantageous, especially for SCC (Self-compacting concrete) with a low fines content (material passing the 0.125 mm sieve).

MasterMatrix SDC 150 can also be used as a pumping aid where difficult materials are being used, or where the pumping requirements in terms of height &/or distance are encountered. In these situations, the dosage rate will need to be assessed on a case by case basis, but would normally be lower than 0.4% by cement (binder) content.

FEATURES AND BENEFITS

MasterMatrix SDC 150 offers the following benefits for the concrete industry:

- Prevents segregation and bleeding
- Can be used with all types of cement
- Does not affect setting times nor early strengths
- Mixes are more robust to changes in water demand
- Can be used as a pumping aid

MasterMatrix SDC 150 consists of a water-soluble polymer which modifies the rheological properties of the mix. The polymer adjusts the viscosity of the paste to obtain the optimum stabilization. MasterMatrix SDC 150 has a dual action:

- It maintains internal cohesion of the concrete during casting
- It resists segregation when the concrete has been placed

DOSAGE

MasterMatrix SDC 150 is batched on the total of fines below 0.1 mm and the normally recommended dosage rate of MasterMatrix SDC 150 is approximately:

- *By Volume* - 0.10 to 0.79 litres per 100 kg of cement (binder) content.
- *By Weight* - 0.10 to 0.80 kg per 100 kg of cement (binder) content.

The dosage rates given above are for typical usages, they are not meant as absolute limits, as other dosages may be utilised in special cases according to specific job conditions. If required consult our Technical Services Department for advice. Trial mixes should be carried out to ensure optimum dosage and effect.

MIXING

MasterMatrix SDC 150 is a ready-to-use liquid admixture, which should be added to the concrete during the mixing process together with the water. This is particularly important in order to obtain maximum efficacy. For best performance, it is advisable to continue mixing until the mix is completely homogeneous.

COMPATIBILITY

MasterMatrix SDC 150 can be used with all types of EN 197 Cements. For use with other special cements, contact our Technical Services Department.

MasterMatrix SDC 150 should not be pre-mixed with other admixtures. If other admixtures are to be used in concrete containing MasterMatrix SDC 150 they must be dispensed separately.
When complimentary admixtures are required it is important that trials are performed, prior to any supply, to

determine the respective dosages of any complimentary admixture, and the suitability, in the fresh and hardened state, of the resultant concrete. In these circumstances, we recommend that you consult our Technical Services Department for further advice.

The rheological behaviour induced by MasterMatrix SDC 150 is optimised when used in combination with MasterGlenium superplasticizer. To produce highly fluid concretes or SCC, MasterMatrix SDC 150 needs be used in combination with a superplasticizer admixture of the MasterGlenium range in order to guarantee maximum efficacy.

MasterMatrix SDC 150 is not compatible with all admixtures of the MasterRheobuild series.

PACKAGING

MasterMatrix SDC 150 is supplied in Bulk, 1000-litre IBC's and 15-litre containers.

CONTACT DETAILS

Master Builders Solutions UK Ltd,
Swinton Hall Road,
Swinton,
Manchester,
M27 4EU
Tel: +44 (0) 161 727 6300
www.master-builders-solutions.com/en-gb

MasterMatrix SDC 150

MASTER® BUILDERS SOLUTIONS

High performance viscosity modifying agent (VMA) for fluid concrete - EN 934-2: T13

Product Data	
Appearance:	Clear liquid
Specific gravity @ 20°C:	1.01 ± 0.01 g/cm³
pH-value:	6.5 ± 1
Alkali content (%):	≤ 0.10 by mass
Chloride content (%):	≤ 0.10 by mass
Segregated portion	≤ 70% of Reference mix
Compressive strength – 28 day	≥ 80% of Reference mix
Air content	≤ Reference mix +2.0%
Chloride content	Max 0.10% by mass
Alkali content	Max 1.0% by mass
Corrosion behaviour	Contains only components according to BS EN 934-1:2008, Annex A.1
Dangerous substances	NPD
Durability	NPD
Logistics	
Shelf life:	12 months if stored according to manufacturer's instructions in unopened container.
Storage conditions:	Store in original sealed containers and at temperatures between 5°C and 30°C. Store under cover, out of direct sunlight and protect from extremes of temperature. Failure to comply with the recommended storage conditions may result in premature deterioration of the product or packaging.
Handling and transportation:	Refer to MasterMatrix SDC 150 Safety Data Sheet
Disposal:	Refer to MasterMatrix SDC 150 Safety Data Sheet

CE

Certificate No. 0086-CPD-469071
EN 934-2: T13
Declaration of Performance can be found at www.master-builders-solutions.com/en-gb

MasterMatrix SDC 150

High performance viscosity modifying agent (VMA) for fluid concrete - EN 934-2: T13

Health and Safety
*For full information on Health and Safety matters regarding this product the relevant Health and Safety Data Sheet should be consulted.

The following general comments apply to all products.

As with all chemical products, care should be taken during use and storage to avoid contact with eyes, mouth, skin and foodstuffs, (which may also be tainted with vapour until the product is fully cured and dried). Treat splashes to eyes and skin immediately. If accidentally ingested, seek medical attention. Keep away from children and animals. Reseal containers after use.

Spillage
Chemical products can cause damage; clean spillage immediately.

DISCLAIMER
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Master X-Seed 100

Hardening accelerating admixture for concrete - EN 934-2: T7

DESCRIPTION

Master X-Seed 100 is an engineered suspension of crystal seeds containing nanoparticles, designed to boost the hydration process of early age cement (6-12 hrs). Based on unique and innovative seeding technology, the growth of the essential Calcium Silicate Hydrate crystals is strongly accelerated.

Master X-Seed 100 promotes concrete hardening at low, ambient and even heat curing temperatures. Unlike traditional acceleration methods and thanks to the unique mode of action - the virtually barrier-free crystal growth of the seeds in between the cement grains - early strength development is accelerated while the final microstructure benefits from equivalent or improved properties.

CRYSTAL SPEED HARDENING

Master X-Seed 100 is the essential component of our Crystal Speed Hardening concept.

Crystal Speed Hardening expresses the Value Proposition offered by the unique crystal seeding technology of Master X-Seed:

- Efficient Processes
- Energy Reduction
- Material Optimization
- High Quality Specifications

The concept addresses key industry requirements and has the power to exceed all current solutions. In particular, the concept is designed to make a significant contribution to meeting sustainable construction targets.

FIELDS OF APPLICATION

Master X-Seed 100 is optimized for all kinds of concretes, especially for structural precast elements where high early strength development is a key success factor for the producer. Master X-Seed 100 is a relevant alternative to heat curing methods and the strong promotion of hydration in particular supports the use of binders with lower clinker content.

FEATURES AND BENEFITS

Master X-Seed 100 offers the following benefits:

- Early strength acceleration at low, ambient and heat curing temperatures
- Flexible adjustment of production capacities
- Increased production cycles (double, triple rotation)
- Better use of formwork by earlier demoulding
- Reduction/elimination of heat curing
- Reduced investment and running cost of curing
- Allows use of minimum required cement quantities
- Allows binder optimization by using lower grade, less clinker-containing cements or by increasing use of supplementary cementitious materials (Limestone, Fly Ash, Slag)
- Lower risk of delayed ettringite formation
- Reduced water absorption
- Improved concrete durability aspects
- Improved plant and product ECO-efficiency by reducing CO_2 emissions

DOSAGE

The normally recommended dosage rate of Master X-Seed 100 is approximately:

- *By Volume* - 0.44 to 5.29 litres per 100 kg of cement (binder) content.
- *By Weight* - 0.50 to 6.00 kg per 100 kg of cement (binder) content.

The dosage rates given above are for typical usages, they are not meant as absolute limits, as other dosages may be utilised in special cases according to specific job conditions. If required consult our Technical Services Department for advice. Trial mixes should be carried out to ensure optimum dosage and effect.

MIXING

Master X-Seed 100 is a ready-to-use liquid admixture to be added to the concrete during the mixing process. Enough mixing time to secure homogeneous dispersion should be provided.

COMPATIBILITY

Master X-Seed 100 can be used with all types of EN 197 Cements. For use with other special cements, contact our Technical Services Department.

Master X-Seed 100

Hardening accelerating admixture for concrete - EN 934-2: T7

Master X-Seed 100 should not be pre-mixed with other admixtures. If other admixtures are to be used in concrete containing Master X-Seed 100 they must be dispensed separately.

Master X-Seed 100 is compatible with all our core technologies such as ZERO ENERGY SYSTEM and SMART DYNAMIC CONCRETE, in particular with

- MasterGlenium type superplastisizers for high fluidification power
- MasterMatrix viscosity modifying agents for robust self-compacting concrete
- MasterAir air entraining agents for improved freeze-thaw resistance
- MasterFinish form release agents for easy formwork removal & aesthetic surface finish.

PACKAGING

Master X-Seed 100 is supplied in Bulk, 1000-litre IBC's and 15-litre containers.

CONTACT DETAILS

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Swinton,
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Tel: +44 (0) 161 727 6300
www.master-builders-solutions.com/en-gb

MASTER®
» BUILDERS
SOLUTIONS

Master X-Seed 100

Hardening accelerating admixture for concrete - EN 934-2: T7

Product Data	
Appearance:	White liquid
Specific gravity @ 20°C:	1.135 ± 0.03 g/cm³
pH-value:	11.0 ± 1
Alkali content (%):	≤ 4.00 by mass
Chloride content (%):	≤ 0.10 by mass
Corrosion behaviour:	Contains only components according to BS EN 934-1:2008, Annex A.1 & declared list A.2.
Air Content:	Fulfilled
Setting time – initial @ 5°C:	≤ 60% of Reference mix
Setting time – initial @ 20°C:	≥ 30 minutes
Compressive strength:	Fulfilled
Durability:	NPD
Dangerous substances:	NPD
Logistics	
Shelf life:	6 months if stored according to manufacturer's instructions in unopened container.
Storage conditions:	Store in original sealed containers and at temperatures between 5°C and 30°C. Store under cover, out of direct sunlight and protect from extremes of temperature. Failure to comply with the recommended storage conditions may result in premature deterioration of the product or packaging.
Handling and transportation:	Refer to Master X-Seed 100 Safety Data Sheet
Disposal:	Refer to Master X-Seed 100 Safety Data Sheet

CE

Certificate No. 0086-CPD-469071
EN 934-2: T6 & T7
Declaration of Performance can be found at www.master-builders-solutions.com/en-gb

Master X-Seed 100

Hardening accelerating admixture for concrete - EN 934-2: T7

Health and Safety
"For full information on Health and Safety matters regarding this product the relevant Health and Safety Data Sheet should be consulted.

The following general comments apply to all products.

As with all chemical products, care should be taken during use and storage to avoid contact with eyes, mouth, skin and foodstuffs, (which may also be tainted with vapour until the product is fully cured and dried). Treat splashes to eyes and skin immediately. If accidentally ingested, seek medical attention. Keep away from children and animals. Reseal containers after use.

Spillage
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